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for January, 1937

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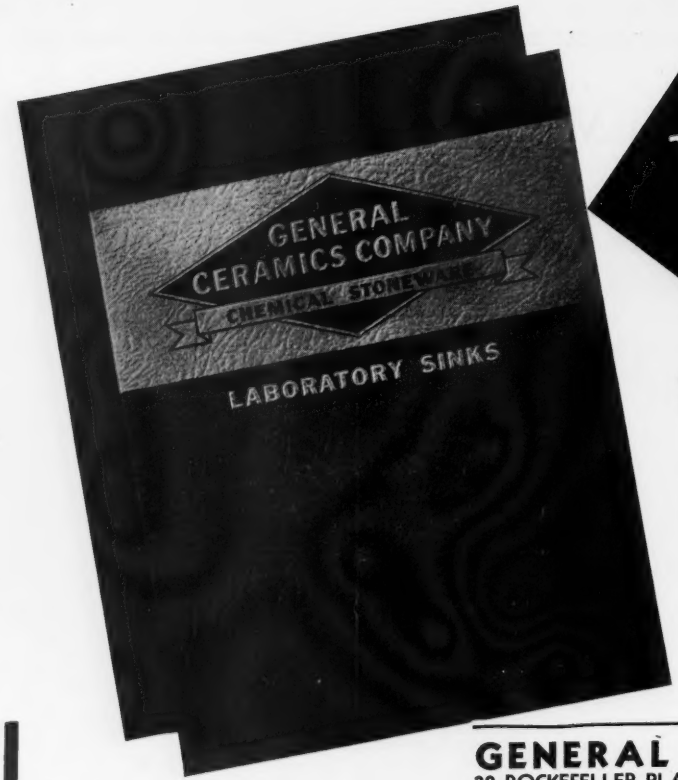

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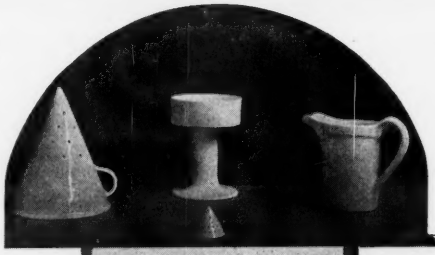

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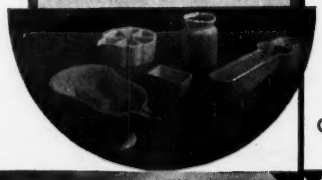

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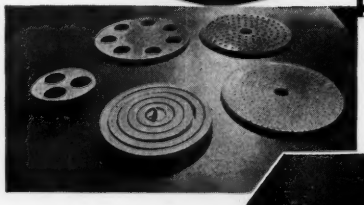

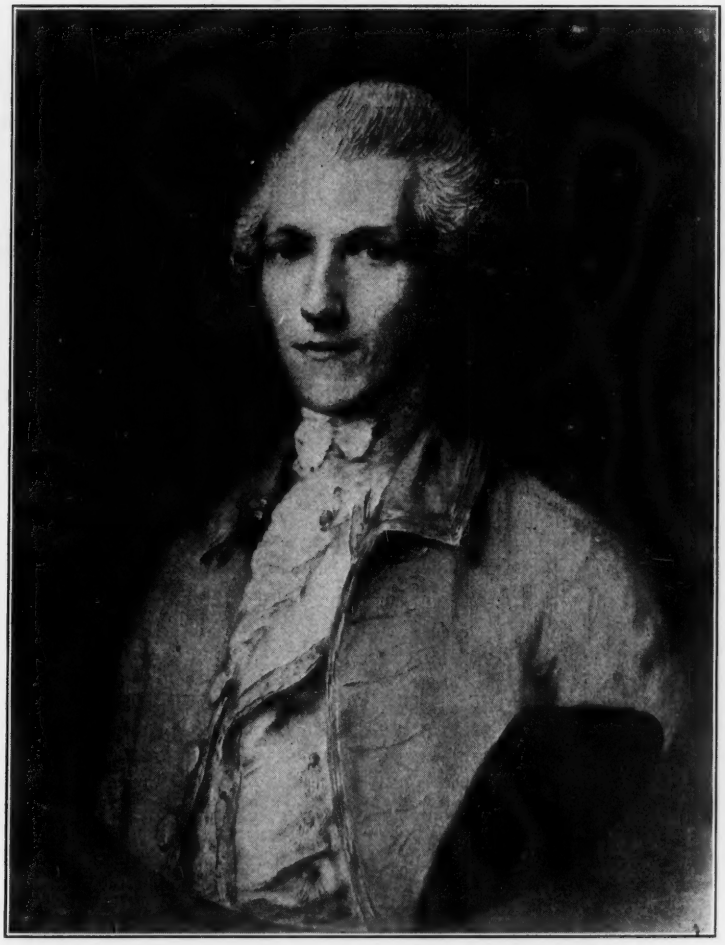

BENJAMIN THOMPSON, COUNT RUMFORD (1753–1814)

This portrait of Count Rumford at the age of thirty, which is considered one of Thomas Gainsborough's finest, hangs in the Fogg Museum of Harvard University. For the photographic copy from which this reproduction was made we are indebted to Dr. Tenney L. Davis.

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EDITOR'S OUTLOOK

THE LYMAN CHURCHILL NEWELL HISTORY OF CHEMISTRY COLLECTION. We take this opportunity to thank the anonymous friend who recently sent us the May, 1936, number of *Bostonia*, the Boston University Alumni Magazine. Of especial interest to JOURNAL OF CHEMICAL EDUCATION readers are the excellent cover portrait of Dr. Lyman Churchill Newell, a brief article by John Philip Mason, describing "The Lyman Churchill Newell History of Chemistry Collection," and a portrait of Mrs. Caroline Strong Newell.

As has been announced in these pages previously, Mrs. Newell has generously turned over to the keeping of the College of Liberal Arts of Boston University Dr. Newell's chemical library (largely historical) and his collection of portraits, letters, manuscripts, and other memorabilia. The collection is housed in the Lyman Churchill Newell History of Chemistry Room in the College of Liberal Arts Building, 688 Boylston Street, Boston. In addition to other necessary furnishings, the room contains Dr. Newell's portrait, his desk, chair, and bookcases, also presented by Mrs. Newell.

The collection was formally opened to visitors on the evening of May eighth last, and since then has been accessible to interested persons by special arrangement with the Department of Chemistry.

Among the interesting items of the collection are copies of the works of Boyle, Stahl, Priestley, Dalton, Lavoisier, and Sir Humphry Davy. There are also letters written by the latter four, as well as by Black, Bunsen, Chevreul, Dumas, Faraday, Kekulé, Liebig, and Wöhler.

Historical scholars and chemists in general are deeply indebted to Mrs. Newell for making available, and to Boston University for safeguarding, this rich store accumulated by Dr. Newell over a lifetime of devotion to a noble avocation. The spirit displayed is characteristic of Dr. Newell himself, for he never hoarded his treasures; he always delighted to share his enjoyment of them with others.

While any of Dr. Newell's students and associates remain he will need no memorial. That his memory remains ever green is attested by the fact that we never attend a national gathering of chemists without hearing anew of the counsel and encouragement that he gave to some former pupil, or of another of the kindly and courteous deeds that endeared him to all with whom he came in contact. We trust that this material memorial may be the means of perpetuating the living memorial that abides in hearts of kindred spirit and in minds of common interest.

HERMANN KOPP, HISTORIAN *of* CHEMISTRY*

JULIUS RUSKA

Institut für Geschichte der Medizin und der Naturwissenschaften, Berlin, Germany

ON FEBRUARY 22, 1892, at Berlin, A. W. Hofmann delivered before the German Chemical Society an obituary address[1] in honor of his friend Hermann Kopp who was to be laid to rest in Heidelberg the next morning. The speaker stressed particularly the pioneer studies that Kopp had systematically carried out over a long period of years in the then new field of physical chemistry. Likewise his services as associate editor of the *Jahresbericht über die Fortschritte der Chemie* and of *Liebigs Annalen* were recalled with well-deserved praise. Of course the gifted orator eulogized Kopp's historical works, but a careful reading of this section of the address leaves the impression that the speaker was here dealing with a topic not quite so close to his heart. T. E. Thorpe,[2] in a special meeting, gave the London Chemical Society an admirable characterization of the deceased German scholar, which was all the more impressive since the speaker had been intimately associated with Kopp and based his text on personal recollections; he discussed the physico-chemical researches in detail, but the historical studies were treated about as they had been by Hofmann. The biographies by Krafft[3] and Bredig[4] also are wanting with respect to an intimate knowledge and competent appraisal of Kopp's accomplishments as an historian of chemistry.

No just blame can be attached to the chemist-biographers of Kopp for their relative neglect of this phase of his activities. A veritable gulf separates the ideology of a modern chemist from the notions prevailing even in the eighteenth century, to say nothing of those current in still earlier periods. Chemical research methods are equally different from the technic employed in philological-historical investigations. Consequently, chemists who are actively practicing their profession either in industry or in research institutes, where the emphasis is on the extension of chemical knowledge, find little reason to turn their attention to historical studies, or, if they do so, they content themselves with paying their respects from afar. Under these circumstances, no criticism can be offered if for once the studies of chemical history that issued from

HERMANN KOPP,
October 30, 1817–February 20, 1892

Kopp's indefatigable pen be considered in somewhat greater detail. The present writer is one of many who received instruction and stimulation from Kopp's historical works and as one of the few remaining who knew him personally,† feels it a pleasant duty to dedicate to that great German savant this essay which will deal primarily with his historical labors and with the investigations that grew out of them. Frau Hofrat Baumann, of Freiburg i. B., Kopp's now aged daughter, kindly furnished some new facts concerning the family.

The name Kopp is rather widely distributed in the Kurhessian states to which the city Hanau belonged prior to the union with Prussia. Johann Heinrich

* Translated by Ralph E. Oesper, University of Cincinnati, Cincinnati, Ohio.

[1] HOFMANN, A. W., *Ber.*, **25**, 505–21 (1892).

[2] THORPE, T. E., "Kopp memorial lecture," *J. Chem. Soc.*, **63**, 775–815 (1893).

[3] KRAFFT, F., "Badische Biographien," **1907**, pp. 406–13.

[4] BREDIG, G., *Allgemeine deutsche Biographie*, **55**, 820–6 (1910).

† Another of Kopp's students, Dr. Alfred Springer of Cincinnati, Ohio, was glad to honor the memory of his revered teacher by defraying certain expenses incurred in the preparation of this paper.

Kopp, the father of the chemist, was born in that city in 1777. He began to practice medicine there in 1802, and later became professor of chemistry, physics, and natural history in the local lyceum. In this capacity and utilizing the resources of an excellent private collection, he published, in part alone, in part with the collaboration of C. v. Leonhard and others, a series of works on mineralogy. He acquired a reputation as a medical writer by issuing "Das Jahrbuch der Staatsarzeneikunde" (1808–20) and "Denkwürdigkeiten in der ärztlichen Praxis" (5 volumes, 1830–45). He declined all invitations to join university faculties, pointing out that the whole city was his clinic. In 1813 he was made Medical Councillor, and later Body Physician to the Kurfürst of Hessia.

Hermann Kopp, born October 30, 1817, had three sisters, no brothers. An only son, and mentally alert, he was naturally given every advantage and care by his father, with the almost inevitable result that he early developed a taste for natural science, particularly mineralogy and chemistry. The aged Goethe once came to see the celebrated mineralogical collection and it was with justifiable pride that Kopp's father presented his son with the words: "Herr Geheimrat, this is the boy who wishes to study chemistry."

The youthful experimentation was doubtless soon buttressed by the discovery of the treasures contained in his father's books. Just as the young Liebig devoured everything on alchemy and chemistry in the Court Library at Darmstadt, so the young Kopp probably had the same passion for reading, and it is quite possible that even as a fifteen-year-old schoolboy he became acquainted with the "History of Alchemy"[5] published in 1832 by Schmieder, professor in the nearby city of Kassel. No special details of the years Kopp spent in the Gymnasium are preserved. The student career at Heidelberg, the doctorate study at Marburg, and the shifting of residence to Giessen, where Liebig had already been teaching for fifteen years, are too well known to need repetition here.

Nothing could demonstrate Kopp's special talent and innate interest in this particular field better than the fact that quite soon after he habilitated in Giessen, he, then only twenty-four, announced a course of lectures on history of chemistry, and only two years later he put out the first volume of his history of chemistry,[6] which he had planned on a quite ambitious scale. It is obvious that the material for an historical presentation of such wide range and such clear-cut organization could never have been assembled in the few years he had been teaching, but the beginning must have been made during his student days. In the preface to this first volume he states that his knowledge of the older textbooks and his early acquaintance with alchemical works had stimulated his interest in historical comparison, and that his more intensive study of the history of the various periods, together with a zealous use of all the other source material available to him had so rounded out his notes that he believed he was justified in publishing them.

No histories of chemistry had been brought out in Germany since those of Wiegleb (1790–92),[7] Gmelin,[8] and Trommsdorff.[9] Meritorious as they were, they yet had grave defects, and furthermore there was now special need of a work dealing with the interrelationships of the various lines along which chemistry had made such tremendous progress since Lavoisier's revolutionary intervention. Thomson's[10] treatment of this topic was not satisfactory, nor did Hoefer's[11] first volume that had just appeared presage much more.

Kopp also points out in his preface that although there is a natural interest in the path along which the science developed as a whole, it is also profitable to study the unfolding of the individual topics that make up chemistry.

The first objective will be practically unattainable and is sure to be submerged in the welter of individual facts and incidental observations that must be included if any attempt is made to unite in a straight succession everything that belongs to the history of chemistry. The problem can only be solved by focusing attention not so sharply on the subject matter of the chemical accomplishments of the various periods, but rather by closely examining the dominant ideas and intellectual tendencies from which these successes evolved. For more than a thousand years chemistry has set for itself general problems, has proceeded along main paths and held appropriate theories; through these many centuries the theoretical views have been joined in a necessary concatenation. The labors of the chemists throughout this whole time were stipulated by the current tendencies, and so they may easily be considered under broad general headings. Treated on these lines, the general history of chemistry presents an uninterrupted, easily comprehended articulated entity.

However, the strivings of chemists may also be considered chiefly with regard to the individual viewpoints which they developed out of their observations and from the standpoint of the positive facts they acquired about certain materials. If this procedure is used, care must be taken not to generalize the resulting conclusions. Only when an effort is made to present the history of each doctrine and each material as a connected individuum does the history of special divisions of chemistry attain its fullest interest. Then, also, the historian can be reasonably sure that he has omitted nothing essential to the understanding of a single topic.

---

[5] SCHMIEDER, K. CHR., "Geschichte der Alchemie," **1832.** Reprinted in **1927.**

[6] KOPP, H., "Geschichte der Chemie," **4 vols., 1843–47.** Reprinted in **1931.**

[7] WIEGLEB, J. CHR., "Geschichte des Wachstums und der Erfindungen in der Chemie in der neuern Zeit," **1790–91.** 2 vols.

[8] GMELIN, J. F., "Geschichte der Chemie seit dem Wiederaufleben der Wissenschaften bis an das Ende des achtzehnten Jahrhunderts," 3 vols., **1797–99.**

[9] TROMMSDORFF, J. B., "Historisches Taschenbuch für Aerzte, Chemiker und Apotheker auf das Jahr 1803 (05)," 3 vols., **1803–06.**

[10] THOMSON, TH., "The history of chemistry," 2 vols., **1830–31.**

[11] HOEFER, F., "Histoire de la chimie depuis les temps le plus reculés jusqu'à notre époque," 2 vols., **1842–43.**

In conformity with these principles, Kopp, in the *General History*, which occupies the first volume of his work, presents the development along the principal lines only, but in addition he points out how the chemical activities were related to the cultural events of the times. The various periods are chiefly portrayed by describing their outstanding representatives. The second volume is then to deal with the history of the accessory sciences and the theoretical doctrines, while the last two volumes are to be devoted to the history of the various groups of materials and single substances.

This plan seemed to Kopp to be the most suitable, even though he knew that it would force him to include in the *General History* certain topics that he would have to discuss again in the special sections, though, of course, from different viewpoints. In one respect he believed himself fitted to render exceptional service: he had studied the preëminent representatives of the various epochs more searchingly than had any of his predecessors. This thorough knowledge of the works of the great discoverers was sure to shed more light on the state of chemistry at their time than could any listing of names and writings whose content, as in Gmelin, was grasped only superficially and utilized accordingly.

In the introduction to the first volume it is pointed out that the history of chemistry discloses characteristics not usually encountered in the other sciences. While these latter disciplines maintain a rather fixed objective, chemistry not only changes its methods and applications but the whole purpose of the science shifts. At one time, the main effort was the transmutation of base metals into gold and silver, later the chief emphasis was on the preparation of medicinals, then came the period of breaking down compounds into simpler materials and the joining of these to reproduce the original compounds. Kopp organized the history of chemistry into five such periods.

The chemical knowledge of the ancients showed comparatively little change over long stretches of time, nor was there much variation over a wide geographical area; no distinct stages of development can be marked off.

The middle history may be divided into two epochs, (*a*) the period of alchemy, which lasted from the fourth to the sixteenth century, that is, somewhat more than a thousand years, and (*b*) the period of medical (iatro-) chemistry, which extended to about the middle of the seventeenth century.

Not until then was the true objective of chemistry recognized and its permanent task made clear. This newer development also took place in two epochs, (*a*) the period of the phlogistic theory, that so clearly put its mark on the 18th century, and (*b*) the period of quantitative studies, which, beginning in the last quarter of the 18th century, have up to now remained dominant in the development of chemistry.

Though the direct benefits arising from an active interest in the history are manifold, Kopp believed that not the least of its values resides in the development of a sane and humanitarian evaluation of the achievements of innovators and non-conformists. "To the strivings of those who put forth their efforts not so much to advance the science as to forward their own personal interests, to those who consider an extension of knowledge important only in so far as they believe themselves entitled to a portion of the credit, to the personal pushing ahead so evident nowadays, to these there can be opposed nothing so effective as the dissemination of the facts of chemical history, which demonstrate to us that no discovery is independent in the full sense of the word, that every one of them is determined by the general spirit of its time, by which it mainly is brought into existence, and in every case the way has been prepared by prior studies. . . . Honor enough remains for those who have won merit by advancing knowledge, even though we see in science an organism that develops independently with representative scholars merely as its organs and not its controllers."

The bounds of this essay make it impossible to discuss also the details and characteristics of Kopp's presentation, or to point out for each individual era its special advantages and occasional defects. However, a few lines will be devoted to several points brought out by a comparison with Hoefer's work.

Kopp kept himself within close limits when he wrote the history of the earliest period, and only Aristotle, Pliny, and Dioscorides are allowed somewhat more space. Even adding all that is mentioned concerning the ancients in the special sections, the total bulks only about one-fifth as large as Hoefer's discussion of the same epoch. The real reason for this glaring difference lies obviously in the fact that Kopp, who was writing a general history, designedly depicted this relatively unfruitful period in a few strokes, in order to have as much space as possible for the later periods. In contrast, Hoefer, who was a universal scholar rather than a chemist,* probably began his work with an extended study of the classical writings, and so was led into a more voluminous presentation.

Striking differences also are apparent in the treatment of alchemy in these two histories, published so closely together. Hoefer, working in Paris, had at hand the great wealth of Greek and Latin manuscripts and the early printed volumes of the Bibliothèque Nationale and so was able to build his history on representative extracts taken directly from both known and unknown texts of the authors whom he wished to characterize. Consequently, for the period of Greek alchemy (of which he gives specimen texts in an appendix) as well as for the period of the translations from the Arabic, Hoefer's discussion is distinctly superior to Kopp's curtailed treatment. On the other hand, Kopp's characterization of the later alchemical period and his discussion of certain general alchemical questions in the

* Ferdinand Hoefer (1811–1878), born at Döschnitz in the Grand-duchy of Schwarzburg-Rudolstadt, at the age of 19 went to France to join the Foreign Legion. He soon tired of this, and became a student of philosophy, natural science, and medicine at Paris.

second volume, in particular the section on the conditions surrounding the alchemists, and the various views concerning the preparation of the Philosopher's Stone, are far better than Hoefer's treatment of these topics.

Both writers are guilty of certain unfortunate errors that were unavoidable, since they were recognized and corrected only at a much later date. An example is the wholly false appraisal of the Latin Geber texts, which were then quite generally accepted as translations from the eighth century Arabic originals. Equally bad was the erroneous dating and evaluation of Basil Valentine, whose putative texts are now known to be post-Paracelsian forgeries. In 1843 Kopp still had practically no knowledge of genuine Arabic writings, but this very ignorance protected him from passing on fantastic statements, such as Schmieder and Hoefer propagated, on the authority of unreliable versions of Latin texts both printed and written.

FOUR PROFESSORS OF CHEMISTRY

BUFF (Giessen) WÖHLER (Göttingen) KOPP (Heidelberg) LIEBIG (Munich)

Photo by Hanfstaengl, Munich, April, 1865. For comments on the better known variant of this photo of these intimate friends, in which Kopp and Buff have changed places, see Schönbein's letter to Liebig in KAHLBAUM'S *Monographieen aus der Geschichte der Chemie*, 5, 191, 194, Leipsic, 1900.

Photo by courtesy of Frau Hofrat Baumann, Kopp's daughter, now living in Freiburg i:B.

Kopp's thorough and understanding treatment of all the subsequent periods, not excepting the iatrochemical era, unquestionably entitle him to first honors. Likewise, the wide scope of the history of the newer chemistry in his first volume demonstrates the indubitable superiority of Kopp's accomplishment. One hundred twenty pages are given over to the phlogistic era, one hundred eighty to the period of quantitative researches, and the development is traced from Lavoisier on to Faraday, Dumas, Berzelius, Wöhler, and Liebig.

It is distinctly worth while to note Kopp's final conclusions, in which he prophetically visualizes the future development of chemistry. He saw a new era appearing, in which chemistry would join more and more closely with the various branches of physics and even with mathematics to form a completed whole. His far-seeing mind would surely have derived a great measure of satisfaction had he lived to see his prediction so strikingly realized in the recent tremendous successes and advances in our knowledge of the atom.

The second volume, which deals with the history of the separate branches of chemistry, needs little comment. It opens with remarks on a variety of topics: the word "chemistry," the earliest textbooks, and the laboratories, apparatus, and working methods that gradually evolved. This section forms the bridge to the history of analytical chemistry which is then carried up to the extension of quantitative analysis. The history of mineralogic, pharmaceutical, and technical chemistry which Hoefer scattered widely over a great many paragraphs, is here compressed by Kopp into 60 pages, but these branches of chemistry are further discussed in the last two volumes where they receive attention adequate to their importance. The remainder of the second volume is given over to the history of the doctrines of chemical affinity, and here again is a brilliant piece of clear, well thought-out exposition, beautifully organized and authentically documented.

The last two volumes must be discussed still more briefly, even though the brilliant way in which Kopp has here arranged and mastered an enormous mass of historical material merits lengthy consideration. Once more, there pass in review the views of the early chemists concerning acids, bases, and salts; once again is recited the story of how the phenomena of combustion and the calcination of metals were by means of the theory of phlogiston welded into a uniform concept which held sway until the discovery that the various gases are fundamentally different brought on the recognition of the true state of affairs. In the third volume the history of oxygen, nitrogen, and hydrogen and their most closely related and simplest compounds is followed by the corresponding sections on sulfur and the halogens. The fourth volume contains the corresponding history of the alkalies and earths, then of the heavy metals, and finally one hundred eighty pages are given over to the divergent topic: "Contributions to the History of Organic Chemistry," which extends through Liebig and Wöhler's studies of bitter almond oil.

The young dozent who had cultivated the historical aspects of his science with so much devotion and success naturally sought to win friends for his beloved subject by lectures. In the winter of 1841–42, in addition to a weekly lecture on meteorology, he lectured twice each week on history of chemistry. This course was repeated in the summer of 1843. Discouraged by the fewness of his listeners, he abandoned this effort and with the single exception of a trial in the winter of

1850-51, he omitted this offering for eleven years. Conditions changed only after 1852 when he became ordinarius at Giessen. Then, regularly each summer, he lectured twice each week on history of chemistry. His other courses were crystallography, including demonstrations with drawings, models, minerals, and chemical preparations, and practical exercises in crystallographic drawing. When he removed to Heidelberg, he followed this same schedule from 1867 to 1890. His only course during the last semester of his academic activity was history of chemistry.

It might be assumed that the extraordinary exertion of compiling the four-volume history would have so exhausted this side of his mental faculties that he would gladly have turned to experimental labors for recreation. In addition, his participation since 1849 in the *Jahresbericht über die Fortschritte der Chemie* and his collaboration since 1851 in the *Annalen der Chemie* would in the case of most men have left no time to even consider further historical works. However, King Maximilian II had asked the Bavarian Academy of Sciences to issue a "History of the Sciences in Germany," and Kopp, probably shortly after he had been called to Heidelberg, was commissioned to write the volume on the development of chemistry in recent times. It is obvious that no one but Kopp could be safely entrusted with so difficult an assignment. That he set to work with renewed vigor is shown by a letter to A. W. Hofmann (April 25, 1865), in which he states that he finally has started the actual writing of his new book.[12] The printed text covers no less than eight hundred forty-five pages, and it is easy to see why Kopp could not finish this gigantic task until 1873 because the account goes about twenty years beyond the bounds of his previous history, *i. e.*, he follows the newer development down to about 1858.

In the preface Kopp points out the grave difficulties that beset the path of the historian who attempts to discuss the rapid succession of ideas which gained acceptance during the period in which he himself has been scientifically active. For at the same time that one party fully accepts certain new views, others pronounce them immature or reject them as misleading speculations, and to do justice in a general history to all these stresses, strains, and opposing viewpoints that mark the course of progress is an immeasurably difficult task. Kopp also regrets that he could not devote more attention to the spread of empirical knowledge, meaning by this the special fields of chemistry and their constantly widened technical applications; this requires special capabilities which he felt he did not possess.

He trusts that he will not be criticized for having dealt at some length with the chemistry of other lands in this history of chemistry in Germany. Chemistry is one of those sciences which neither in subject matter nor in form belongs exclusively to one nation. What had recently been accomplished in Germany was made possible only by the closest give-and-take with the discoveries made in other countries. It is the bounden duty of the historian to show himself as owing allegiance to no particular homeland; he must be a man without a country. Nothing could be falser than to interpret this warning of objectivity as the expression of a secluded or indifferent mind. It is purely a renunciation of that chauvinistic spirit which on the other side of the Rhine had led to the claim that chemistry is a French science. The evaluation of the total accomplishment in a science is not concerned with individual nationalities; in scientific fields at least it is reasonable to expect an effort to secure a measure of objectivity proportionate to the dignity of the theme.

Thorough as usual, Kopp began by laying a firm foundation for his history of the newer chemistry. In this introduction, with a few strokes he portrays the early chemistry up to Boyle, then follows a somewhat more extensive treatment of the developments during the seventeenth and eighteenth centuries, and finally the reformation by Lavoisier. This latter chapter in which is told the story of the overthrow of the phlogistic hypothesis is most excellent and enjoyable reading, but it also demonstrates Kopp's unwavering impartiality. At its close he discusses the painful duty laid upon the historian of bringing into his delineation of Lavoisier the shadows which unfortunately were not lacking in the career of this brilliant scientist; the evasion of this obligation would be tantamount to depriving others of their just due. The critical remarks that Kopp felt it necessary to add to the discussion of the merits of Dalton (p. 287) and Berzelius (pp. 315 *ff.*, 625 *ff.*) should also be read with this point in mind.

In the succeeding larger sections dealing with (1) the extension of the atomistic theory and the determination of atomic and molecular weights, (2) the expansion of inorganic chemistry and the revamping of the chemical system, (3) the development of the ideas concerning organic compounds and the refutation of the previous views, the year 1840 is repeatedly made the turning point of Kopp's observations. This was the time at which the fundamental discoveries of Dumas, Liebig, Laurent, and Gerhardt finally ousted the electrochemical system of Berzelius, especially from organic chemistry. 1840 is also the year with which Kopp in 1843 closed the first volume of his "History of Chemistry." In contrast to his previous presentation of the "Period of Quantitative Researches," which was then compressed into a single section of one hundred eighty-five pages, this topic was here expanded into eight chapters totaling about five hundred pages. This period of decisive conflicts had now been made the heart of the entire work. The later development is treated under the headings: "Recollection of Several More Important Advances in Chemistry up to about 1858," and "Development of the Newer Theories of the Chemical Constitution of Compounds." As these two chapters together occupy no more than two hundred pages, it is patent that this compressed discussion is inadequate, considering the importance of the topic.

[12] KOPP, H., "Die Entwickelung der Chemie in der neueren Zeit." Also under the title: "Geschichte der Wissenschaften in Deutschland. Neuere Zeit," Vol. X, 1873.

Kopp repeatedly (pp. 632, 649, 705, etc.) felt impelled to call attention to the enormous difficulties of the task; he no longer had the power completely to master the assignment. It is a fair question whether any individual living today feels competent to write a corresponding exhaustive account of the seventy-five years of chemical history that have since intervened, even though, like Kopp, he limited his discussion to the changes in general viewpoints and the advances in methods.

A remarkable change in Kopp's literary style is revealed by even a cursory comparison of the first part of his four-volume history with his "Development of Chemistry in Recent Times" written thirty years later. The young author wrote few passages that are difficult or require rereading because of involved, heavy construction. The language is simple, bright, fresh, and certain peculiarities foreshadowing Kopp's later style will strike only those who are already familiar with the ponderous passages, the endless periods, the complicated structures of the protracted statements so characteristic of the older man. This style of his later years is so peculiarly his own and so unmistakable that practically all of Kopp's biographers have commented on it. A. W. Hofmann's belief that Kopp produced these extraordinarily long periods in an endeavor to be concise is too paradoxical to deserve much credence; it is much more plausible to ascribe this change to Kopp's absorption in the Latin writings of the philologists and alchemists of the preceding centuries. If this immersion in the old writers is not the complete explanation, the ultimate reason doubtless lies in the predispositions of Kopp's character, in his almost painful conscientiousness and in his striving to exhaust all possibilities and to do justice to all points of view.

The notes of his university course have been preserved and they show that this meticulous, rather solemn style was not always absent even when he was lecturing to students. However, it would be entirely false to conclude from this that in his letters or in personal conversation he likewise clothed his thoughts in these heavy academic hangings. Thorpe's spirited description of the man whom he had learned to know through intimate association rounds out the picture of this gifted mind and recreates Kopp once again as a living figure:

"To know Kopp was to love him. . . Kopp's colloquial powers were admirable; like the Great Lexicographer, he loved to fold his legs and have his talk out. His strong common sense; his vigorous, incisive thought; the range of his information of men and letters; his quick, retentive memory, his felicity of expression; his fund of anecdote; his ready wit and genial humour—all made him delightful to listen to. To watch the play of his features as he talked was in itself a recreation. Every line in the quaint, impressive face was instinct with intelligence, the outward and visible sign of the active restless 'geist' behind it. Not that there was any sense of unrest about the man. When I first knew him, a quarter of a century ago, he may be said to have passed the noontide of his intellectual career; it was the quiet, contemplative post-meridian life of a philosopher whose period of active service as a researcher was well nigh spent, happy in his surroundings and in his occupation; his social sympathies satisfied by his relations with colleagues like Bunsen, Kirchhoff, Helmholtz, Renaud, Königsberger, and Zeller; and his mental activity finding scope for itself in his lectures, in the exercise of the various offices connected with the management of the University which he was called upon to fill, and in his literary labours."[13]

The second domain of historical studies to which Kopp indefatigably applied himself in a zealous effort to exhaust the available material brought him no less fame than did his volumes on the history of chemistry. This section of his researches is made up of his various contributions to the history of alchemy.

Alchemical literature exercises a peculiar charm, and anyone who has ever fallen under this spell readily understands why Kopp turned his attention again and again to these preliminary stages of chemistry. He doubtless was led to his numerous supplementary studies by the many unsolved literary problems, by the uncertainty and contradictions of the early writings, and by the incomprehensibility of many of the documents that claimed to be repositories of divine wisdom. Schmieder's painstaking and comprehensive account of the history of alchemy, although the best that had as yet appeared, could make no claims to be viewed as a critical work of the caliber needed by the progressing science. Likewise, a study of Hoefer's text made it quite apparent to Kopp that a real history of alchemy could never result from the methods used by this writer who attempted to produce a picture of medieval alchemy by singling out passages from the literature and attaching to them divers fantastic interpretations.* Kopp repeatedly found that no reliance could be placed on second- and third-hand assertions, that he had to consult the original literature to arrive at his own decisions. Consequently, even at Giessen, and likewise later at Heidelberg, Kopp put forth all his remaining energy to collect, winnow, and critically revolve in his mind all that the scholarly humanists, polyhistorians, and chemists of the sixteenth to the eighteenth century thought they knew about the Greek, Arabic, and Latin sources of alchemy.

It might be asked if this labor was necessary, whether Kopp would not have used his time to better advantage in personally disinterring the source material from the dust of the libraries and making it available to all. The mere putting of this question would demonstrate that the inquirer has no acquaintance with the difficulties that beset the realization of this wish, obstacles that still exist. It is true that since 1888 the most important Greek texts have been available in an edition put out by Ch. E. Ruelle at the instigation of Berthelot,[14] but it is well known that this edition is not done carefully, it is inadequate, and falls quite short of meeting more exacting requirements. The still more important Arabic sources will not be accessible until several generations of Orientalists have expended much arduous labor.

[13] THORPE, T., *loc. cit.*, pp. 776 *ff.*

* See, for example, note 256, p. 341 of KOPP'S "Beiträge" (reference 15).

[14] BERTHELOT, M. AND RUELLE, CH. EM. (Editors), "Collections des anciens alchimistes grecs," 1887–88.

The studies which Kopp, in 1869, published in two continuously paged sections entitled "Contributions to the History of Chemistry"[15] deal exclusively with the Greek alchemists. It is truly astounding to note what he has brought together here—material from the most remote sources, from learned publications, excerpts from earlier writers, items from library catalogs, and withal he separates the chaff from the grain with critical understanding. If, with pen in hand, this volume is studied and compared with any more recent treatment, the inevitable conclusion is that as regards interpretation of the texts and classification of the authors, Kopp's accomplishment, in essence, has not been surpassed even today. No one can discuss the Greek alchemists without having given serious consideration to the critical researches found in these "Beiträge." Kopp's compilation (pp. 243–365) was until quite recently, *i. e.*, until the publication, 1924–32, of the catalog volumes of the Union Académique Internationale, the sole reliable basis for the study of the Greek alchemical manuscripts.

The third portion of Kopp's "Beiträge," published in 1875,[16] contains a long section entitled: "Views concerning the task of chemistry and the fundamental constituents of materials held by the more prominent chemists from Geber to G. E. Stahl." He here discusses iatrochemists and their successors and reaches conclusions about their achievements and true place in chemical history that rest on much firmer foundations than did judgments pronounced by any of his predecessors.

One particularly great advance was that at last Kopp here makes an excursion into the Arabic literature. To be sure, he does not always utilize the best authorities, yet none of the great bibliographic and biographic works of the Arabs is missing, access to these being given to him by the translations and commentaries of Hammer, Wüstenfeld, Flügel, de Slane, etc. Unfortunately, he added a series of interminable notes in comparison with which the text practically disappears. To the average reader this maze of remarks concerning Khalid, Ja'far, Jabir, and other alchemists is inextricable, and even Kopp did not make full use of the material he assembled, for it contained everything necessary to a solution of the Geber problem.

Through Hammer's translation, Kopp already knew the whole content of the article devoted to Jabir in the "Fihrist" of Ibn an-Nadim and all the book titles mentioned by Hajji Khalifa. He also pointed out that he had found no convincing evidence that any of these works might be the original of one of the books circulating in the Occident under Geber's name. He gives accurate information about the Arabic Geber manuscripts in the European libraries, especially those in Paris, Leyden, and London; his data concerning manuscripts and printed editions of the Latin Geber texts are quite detailed. He was assured by his colleague, Gustav Weil, a competent Orientalist, that Geber's "Summa" contains not a shred of evidence that this work had been translated from an Arabic original. And yet, with the backing of all these facts, he could not muster up sufficient courage to draw the only possible conclusion and to expose a literary fraud that had led the history of chemistry astray for five centuries.

KOPP'S GRAVE IN THE WALDFRIEDHOF, HEIDELBERG

Kopp's critical review of "De Anima," alleged to be the work of Avicenna, was more decisive, but details cannot be given here, nor of his analysis of the writings of the great scholastics. Despite the accumulation of a vast mass of material on which he expended much penetrating discrimination Kopp came to no definite opinion about the Basil Valentine problem, but contented himself with the comment that more can be said in favor of than against the view that these texts date from not before, but after Paracelsus.[17] The repeated study of source materials considered from new angles led Kopp to characterizations of the chemists of the

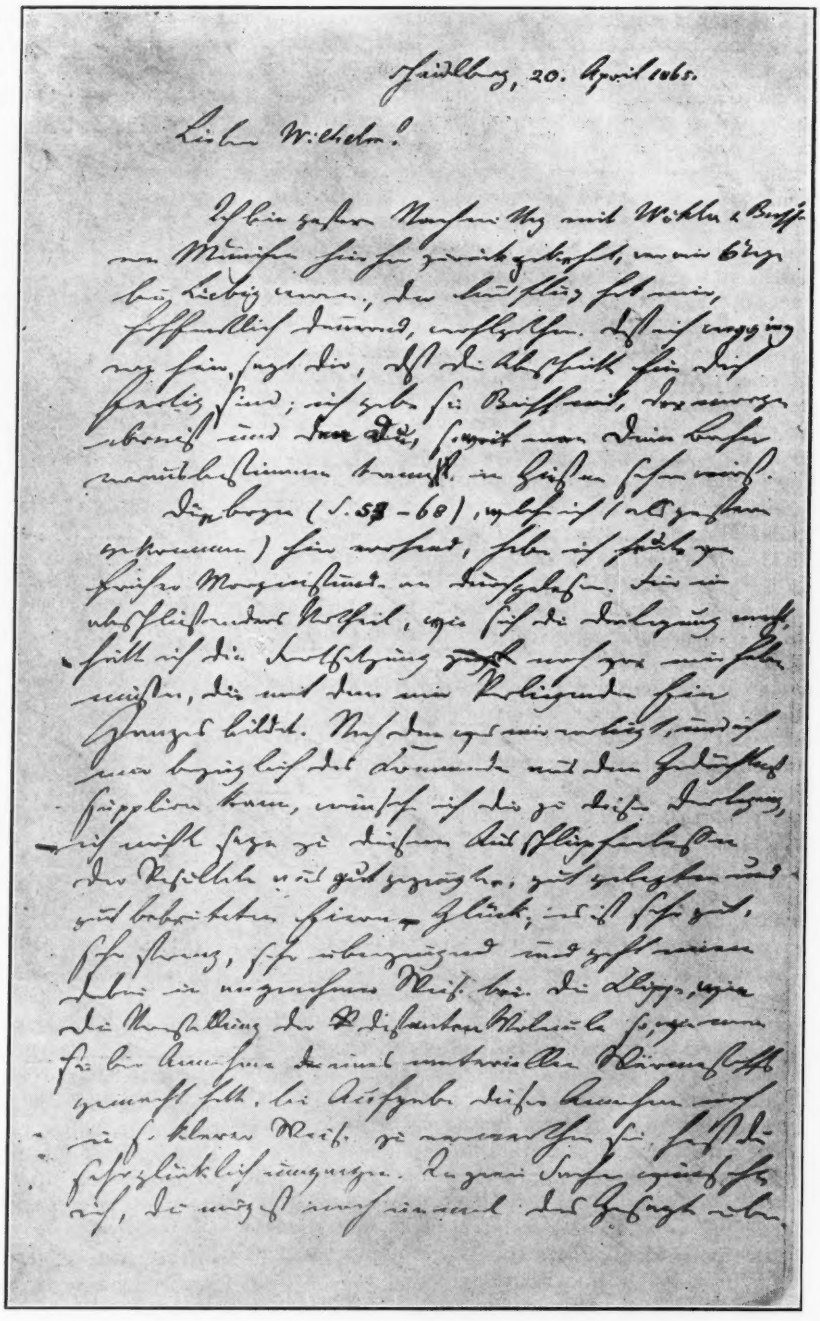
[15] KOPP, H., "Beiträge zur Geschichte der Chemie," Parts 1 and 2, 1869.

[16] KOPP, H., Part 3 of "Beiträge" also carries the title: "Ansichten über die Aufgabe der Chemie und über die Grundbestandtheile der Körper bei den bedeutenderen Chemikern von Geber bis G. E. Stahl. Die Entdeckung der Zusammensetzung des Wassers," 1875.

[17] Compare the chapter: "Basilius Valentinus" by F. FRITZ in BUGGE'S "Das Buch der grossen Chemiker," vol. 1, Verlag Chemie, Berlin, 1929, p. 125.

seventeenth and eighteenth centuries that cannot be more than mentioned here. The closing discussion, which deals with the discovery of the composition of water, must also be treated with the same summary brevity.

At the celebration of the jubilee of Heidelberg University in 1886, Kopp, then almost 70, published another work on the history of alchemy. This, his last long publication, like its predecessor, is no continuous, well-balanced production, but consists of a loose collection of monographs and notes, which Kopp prepared for publication to save them from being lost. The work,[18] in two separately paged parts, bears the title: "Alchemy in earlier and more recent times. A contribution to the history of culture." The first part takes alchemy up to the last quarter of the eighteenth century, the second treats of its vicissitudes from then on. The sub-title indicates that this is an attempt to portray alchemy, not as a preliminary stage of chemistry, but as a chapter in general intellectual development, that is, stress is laid on its philosophical, religious, social, and especially psychological implications and effects. This intention is particularly obvious in the first part, which is definitely a history of the alchemical faith. Kopp shows how the utterances of recognized authorities spread a protecting mantle over the belief that gold can be made artificially and that the philosopher's stone actually exists; he points out how such sponsorship held up the hands of the persevering workers during their laborious efforts to reach these elusive



A SPECIMEN OF KOPP'S HANDWRITING

This letter, April 20, 1865, to Kopp's fellow student and dear friend, A. W. Hofmann, begins: "Yesterday afternoon, I together with Wöhler and Buff returned here from Munich where we spent 6 days with Liebig." Concerning this visit, Liebig wrote to Schönbein: "Wöhler, Buff and Kopp were with us a week at Easter, we had a fine time together as you can see from our faces." See group portrait reproduced on page 6.

This letter is reproduced by courtesy of A. W. Hofmann's daughter, Frau Irmgart von Gagern.

[18] KOPP, H., "Die Alchemie in älterer und neuerer Zeit. Ein Beitrag zur Culturgeschichte," 2 vols., 1886. Erster Theil: "Die Alchemie bis zum letzten Viertel des 18ten Jahrhunderts." Zweiter Theil: "Die Alchemie vom letzten Viertel des 18ten Jahrhunderts an."

goals, he tells how the firm faith in the healing powers of the stone brought enthusiastic disciples to alchemy even as late as the nineteenth century.

Another section deals with the support of alchemy by the temporal and ecclesiastical nobility, who hoped to improve their finances through the services of either itinerant adepts or of court alchemists whose salaries, sometimes small, sometimes generous, were often entirely suspended by the hangman into whose hands the goldmakers sometimes were delivered when the patron's patience was finally exhausted. The exposure of even the grossest frauds could not shatter the belief in alchemy, nor could the warnings of occasional skeptics be any more effective, so long as alchemy found support in an ever closer union with orthodox bigotry, cabalistic excesses, and Free Masonic secret doctrines. This is brought out with special clearness in the history of the Rosicrucians whose deranging mental influence is exposed in detail in the case of G. Forster and S. Th. Sömmerring. A history of the Hermetic Society founded by Kortum and Bährens, and a discussion of several of the more reputable nineteenth century defenders of alchemy close this section. In the light of present developments it is quite interesting to recall the arguments which A. Helfferich, in 1857, brought to the defense of alchemical doctrines: "That chemistry as a science cannot permanently content itself with a purely accidental multiplicity of so-called elementary materials of which some that today are held to be simple, will by tomorrow prove to be compound, must be obvious to everyone who, even partially, values the intuitive striving of the human mind for unity, and who is not altogether deaf to the historical teachings of chemical analysis."

A series of digressions, called notes, fills a further hundred pages. The most important of these are the supplements to the *Aurea catena Homeri*, a subject on which Kopp had previously put out a short paper,[19] and a memoir dealing with alchemy in Austria and its relations to the cabala. At the end comes a ninety-page "Contribution to the Bibliography of Alchemy," one of the most delightful sketches that has ever been written about the verbose book titles of the pseudo-science that had come to be the rendezvous of dupes, bigots, and cheats. These bombastic, grotesque, inelegant, and incomprehensible titles need only be read to demonstrate why this literature perished under the weight of its own ridiculousness.

At the close of his discussion of nineteenth-century alchemy, Kopp gives a review of the recent works on the history of alchemy. He begins with a characterization of Schmieder's book which he calls a report on the persons and writings concerned with alchemy, "worked up with great diligence, little critical sense, and rather much credulity." Everybody knows that Schmieder actually believed that certain alchemists had been successful. Though a disbeliever in his younger days, at the age of forty he came upon facts that gave him pause and after an extended study of the literature he became convinced that certain adepts such as Setonius, Wagnereck, Laskaris, etc., had worked with actual goldmaking preparations. Kopp's opinion was that Schmieder had come to this decision while under the influence of "pseudopsia," a failing that afflicts many historians, particularly those who write on political fields, namely, they see only those things that agree or seem to agree with their preconceived notion, while everything discordant is seen incompletely, distorted, or not at all.

Hoefer was praised because the first part of his "Histoire de la Chimie" considerably extended the information on the Egyptian school whose alchemistic treatises were for the most part available only in transcript. Kopp points out that Berthelot, in his "Origins of Alchemy,"[20] increased this knowledge to a still greater extent by studying the connection of the theories of the alchemists with the philosophical doctrines of the ancients. The works of Chevreul, Figuier, Rodwell, and Ferguson were also referred to explicitly.

A half century has passed since Kopp's last great work appeared and it seems proper that his work should in its turn be critically reviewed. What has been the effect of his writings, how much is out of date, what part has remained alive? Since the present writer's own researches have dealt primarily with alchemy, it seems best to limit the discussion to this field.

Consideration should be given first to Berthelot, who, aided by classical philologists and orientalists, brought out texts and translations and thus put the history of alchemy upon an entirely new foundation. The volumes of the "Collection des Alchimistes Grecs" that appeared while Kopp was still living, together with the three later volumes,[21] ushered in a new era in the study of alchemical history These not only made the Greek alchemists and the first Syrian and Arabic texts accessible, but their brilliantly written prefaces and historical comments greatly enhanced their value to students.

Since Kopp, more than any of his contemporaries, knew how scanty was the information on early alchemy, there is point in the question as to why he did not take this decisive step, why he had not enlisted the coöperation of German philologists and orientalists in the publication of these indispensable texts. The reasons for his failure to do this are not far to seek. Where in Germany could Kopp have found philological collaborators willing to undertake so minor a task as putting out alchemical texts? And where was he to procure the funds to defray the expenses of issuing volumes whose importance patently would be recognized by only a narrow circle of scholars? He was a provincial German professor receiving less than a modest income, he was not like Berthelot, situated in the very center of the

[19] KOPP, H., "Aurea catena Homeri," 1880, p. 50. Dedicated to Wöhler in honor of his 80th birthday.

[20] BERTHELOT, M., "Les origines de l'alchimie," 1885.

[21] BERTHELOT, M., "La chimie au moyen âge," 3 vols., 1893. Vol. 1, "Essai sur la transmission de la science au moyen âge. Traditions techniques et traductions arabico-latines, etc." Vol. 2, "L'alchimie syriaque, etc." Avec collaboration de RUBENS DUVAL. Vol. 3, "L'alchimie arabe, etc." Avec collaboration de O. HOUDAS.

intellectual life of a brilliant capital, he was not at the head of institutions that showered upon him the highest honors and laid at his feet ample funds for all his enterprises.

No one will deny that Berthelot's works are still an indispensable basis for researches in the history of alchemy and that, as examples of what could be done, they affected the course of later developments. But was it necessary for Berthelot to create the impression that he was the first and only scholar who had studied early alchemy, and was there any occasion for his coolly disavowing his indebtedness to the work of Kopp and Hoefer? And did he not by his positive, self-assured presentation engender the belief that all the problems relating to early alchemy had been cleared up and permanently solved by him?

Be that as it may, it is a striking fact that with the death of Berthelot all research in the field of alchemical history seemed also to have perished. Many years passed in which nothing more was done, and in wide circles it was the custom to regard Berthelot's pronouncements as the final word. Not until E. O. von Lippmann published his monumental volume on the origin and spread of alchemy[22] was the spell that had been cast over this field of historical study broken, and the scientific investigation of the history of alchemy revived. Von Lippmann's exemplary conscientious use of source materials has regained for the earlier historians, especially Kopp and Hoefer, their rightful prestige; his incorruptible sense of justice has put Berthelot's chauvinistic claims back into their proper limits. From von Lippmann's works have issued the stimuli that prepared the way for the historical research of today.

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The foregoing has been an attempt to portray the life work of a scholar, whose delightful personality was displayed in his letters to his friends and in his animated intercourse with his colleagues and students, rather than in the labored, stilted, and long-drawn-out sentences of his historical writings.

A fitting and agreeable task has long needed doing: the publication of his letters, particularly those to his closest friends, Liebig, Wöhler, Bunsen, and A. W. Hofmann. This collected correspondence would be an appropriate and well-merited biographical memorial to that gracious character, Hermann Kopp, learned scholar, eminent chemist, first-rate historian, respected teacher, beloved friend.

[22] VON LIPPMANN, E. O., "Entstehung und Ausbreitung der Alchemie," Julius Springer, Berlin, Vol. I, 1919, Vol. II, 1931.

A CHEMIST LOOKS *at* CULTURE

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A COLLEAGUE, in a polished address, years ago informed us that a man of culture should know his Homer and his Aeschylus, his Cicero and his Virgil, his Dante and his Tasso, his Milton and his Shakespeare, his Goethe and his Schiller, his Cervantes and his Ibanez—and many more. We may doubt whether he included Poe and Bret Harte, Walt Mason, and Marcus Whitman. His western frontier of culture was evidently the Atlantic Ocean.

Doubtless this list was intended to leave chemists with an enduring sense of shame. But is culture really only literary? The very next lecture we attended seemed to imply that it is artistic. If you remark, "That must be the 'Moonlight Sonata'," and get the reply, "No, it's the 'Humoresque'," you will know by the tone of your informer's voice that he considers that you have no culture.

You reveal your culture or lack of it in the remarks you make when visiting an art gallery. It is a painting, let us say, of a garbage can, labeled "Still Life." Don't question its right to be exhibited. It must be right artistically or it wouldn't be there. If you have culture you may speak of the balance, plastic quality, mass, or color tonality of that garbage can; or you may say that it has atmosphere.

Thus you may conclude that culture consists in knowing how to use the words that are technically correct in speaking of things that are supposed to mark culture, "If you haven't art, just play the part; it really doesn't matter, if you can only join the patter." It may occur to you that the reason chemistry is not supposed to be cultural is that it does not lend itself to patter. At any rate, we get the impression from these literary and artistic people that culture is something peculiar to themselves and which chemists should at least wish they possessed, though its acquisition is denied them.

But, seriously speaking, is culture limited to things literary and artistic? What is the place of history and philosophy? What about the scientific world? And so for other fields of human effort. What is culture, after all? It is significant that our literary and artistic friends never speak of definite things you must know in order to be rated as cultured. They seem to be looking for a certain quality and state of mind. Culture is evidently concerned with capacity for emotion and

capacity for thought. We acquire it in proportion to the broadening of our mental and emotional capacities and experiences. Culture is not something gained from without, but something developed within. Other minds at best may only catalyze this process. At worst, they may retard it. Most people read too much. The attainment of culture demands purposeful reading, with definite objectives, and the understanding that much that other people would have you read is not worth while for you.

True culture has a wide horizon. It is an escape from our own little cell of the space-time continuum. It concerns the attainment of an eminence from which we may survey the intellectual achievements of the human race in our own time and in former times. This demands historical perspective. We glimpse our savage ancestors, clothed in skins, in the distant Age of Stone. We see the early beginnings of agriculture, then of architecture. We hear the crack of slave drivers' whips at the building of the Pyramids. We catch the flash of Phoenician oars on voyages beyond the Pillars of Hercules, venturing thousands of miles to secure amber, tin, and mercury in exchange for glass, niter, papyrus, and Tyrian purple, the products of the chemical industries of that day. We see Roman armies on the march, see Rome overwhelmed by the barbarians, and note how slowly civilization recovered from that blow and how late in the story of mankind were the beginnings of science. Then comes the scientific age, the world transformed by a new mode of thought!

The literary and artistic achievements of mankind are but a slight part of our heritage from the past. Man existed on earth for thousands of generations before he began to leave written records. Our chief debt to the past is in our control over the forces of nature. To learn how this was won, what problems man has met and overcome in winning food, shelter, clothing, and leisure—surely this is an element of culture. My appeal is for cultural contacts that are broader than those usually suggested. The masterpieces of art and of literature are the products of the creative intellect in directions in which imagination may take almost what course it will. But science, too, has its masterpieces. The story of their development is the story of how wonderfully the material resources of the earth have been multiplied, which we learn just by looking attentively at things about us and by reflecting about them. The creative intellect here encounters unyielding reality. Imagination still plays the predominant part that it does in art and literature, but it must square its course between the headlands of fact.

Then, may we not add other names to the roster of those whose minds, by stimulating our minds, may develop within us the capacities that we have called culture? May we not maintain that the man of culture should know his Newton and his Leibnitz, his Darwin and his Mendel, his Copernicus and his Herschel, his Kelvin and his Helmholtz, his Planck and his Einstein, his Kekulé and his Mendeléef?

Again, our program calls for contact with minds, rather than with facts. The most amazing things in science are not the facts that science has brought to light, but the means by which they were obtained, expeditions of the exploring intellect beyond the frontiers of knowledge, bold flights into the realm of the unknown. Atoms and molecules, protons, and electrons, quanta and cosmic rays—marvelous, all of them; but the crowning marvel is that the human mind ever penetrated so far beyond the limits of the unaided human senses.

As students of chemistry you may make contact with other minds in most of the fields of intellectual and artistic effort. The chemist determines the composition of the concrete and steel of which our public works are built. In this field of common interest he meets the architect and the civil engineer. He creates new medicines for the cure of disease, or synthesizes new anesthetics. Here he meets the bacteriologist, the physician, the pharmacist, the physiologist, the biologist. He studies reactions taking place in crucibles and test tubes, and draws conclusions concerning the manner in which minerals come into being in the depth of the earth. Here he meets the geologist, the mineralogist, and the mining engineer.

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He considers the effect of varnish on the quality of a violin, or the slow disintegration of written records under the influence of the atmosphere. Here he meets the musician, the business man, the printer, and the librarian. He passes the starlight through the prism of his spectroscope, and draws conclusions regarding the composition of worlds in distant depths of space. Here he meets the physicist, the mathematician, and the astronomer.

Of course, none of us specializes in directions that will make all of these contacts possible. We have merely shown how manifold are the opportunities that the chemist has for cultural development. What any man becomes is determined by what there is within himself to be unfolded to the light of day, and how alert he is to his opportunities for self-development. There are chemists, unfortunately, whose interests extend no farther than the fumes and reek of their own laboratories. The teacher of chemistry, nevertheless, may show that our science has contact with most other human interests. The more widely we have

intellectual life of a brilliant capital, he was not at the head of institutions that showered upon him the highest honors and laid at his feet ample funds for all his enterprises.

No one will deny that Berthelot's works are still an indispensable basis for researches in the history of alchemy and that, as examples of what could be done, they affected the course of later developments. But was it necessary for Berthelot to create the impression that he was the first and only scholar who had studied early alchemy, and was there any occasion for his coolly disavowing his indebtedness to the work of Kopp and Hoefer? And did he not by his positive, self-assured presentation engender the belief that all the problems relating to early alchemy had been cleared up and permanently solved by him?

Be that as it may, it is a striking fact that with the death of Berthelot all research in the field of alchemical history seemed also to have perished. Many years passed in which nothing more was done, and in wide circles it was the custom to regard Berthelot's pronouncements as the final word. Not until E. O. von Lippmann published his monumental volume on the origin and spread of alchemy[22] was the spell that had been cast over this field of historical study broken, and the scientific investigation of the history of alchemy revived. Von Lippmann's exemplary conscientious use of source materials has regained for the earlier historians, especially Kopp and Hoefer, their rightful prestige; his incorruptible sense of justice has put Berthelot's chauvinistic claims back into their proper limits. From von Lippmann's works have issued the stimuli that prepared the way for the historical research of today.

* * * * * * * * *

The foregoing has been an attempt to portray the life work of a scholar, whose delightful personality was displayed in his letters to his friends and in his animated intercourse with his colleagues and students, rather than in the labored, stilted, and long-drawn-out sentences of his historical writings.

A fitting and agreeable task has long needed doing: the publication of his letters, particularly those to his closest friends, Liebig, Wöhler, Bunsen, and A. W. Hofmann. This collected correspondence would be an appropriate and well-merited biographical memorial to that gracious character, Hermann Kopp, learned scholar, eminent chemist, first-rate historian, respected teacher, beloved friend.

[22] VON LIPPMANN, E. O., "Entstehung und Ausbreitung der Alchemie," Julius Springer, Berlin, Vol. I, 1919, Vol. II, 1931.

A CHEMIST LOOKS *at* CULTURE

H. G. DEMING

University of Nebraska, Lincoln, Nebraska

A COLLEAGUE, in a polished address, years ago informed us that a man of culture should know his Homer and his Aeschylus, his Cicero and his Virgil, his Dante and his Tasso, his Milton and his Shakespeare, his Goethe and his Schiller, his Cervantes and his Ibanez—and many more. We may doubt whether he included Poe and Bret Harte, Walt Mason, and Marcus Whitman. His western frontier of culture was evidently the Atlantic Ocean.

Doubtless this list was intended to leave chemists with an enduring sense of shame. But is culture really only literary? The very next lecture we attended seemed to imply that it is artistic. If you remark, "That must be the 'Moonlight Sonata'," and get the reply, "No, it's the 'Humoresque'," you will know by the tone of your informer's voice that he considers that you have no culture.

You reveal your culture or lack of it in the remarks you make when visiting an art gallery. It is a painting, let us say, of a garbage can, labeled "Still Life." Don't question its right to be exhibited. It must be right artistically or it wouldn't be there. If you have culture you may speak of the balance, plastic quality, mass, or color tonality of that garbage can; or you may say that it has atmosphere.

Thus you may conclude that culture consists in knowing how to use the words that are technically correct in speaking of things that are supposed to mark culture, "If you haven't art, just play the part; it really doesn't matter, if you can only join the patter." It may occur to you that the reason chemistry is not supposed to be cultural is that it does not lend itself to patter. At any rate, we get the impression from these literary and artistic people that culture is something peculiar to themselves and which chemists should at least wish they possessed, though its acquisition is denied them.

But, seriously speaking, is culture limited to things literary and artistic? What is the place of history and philosophy? What about the scientific world? And so for other fields of human effort. What is culture, after all? It is significant that our literary and artistic friends never speak of definite things you must know in order to be rated as cultured. They seem to be looking for a certain quality and state of mind. Culture is evidently concerned with capacity for emotion and

capacity for thought. We acquire it in proportion to the broadening of our mental and emotional capacities and experiences. Culture is not something gained from without, but something developed within. Other minds at best may only catalyze this process. At worst, they may retard it. Most people read too much. The attainment of culture demands purposeful reading, with definite objectives, and the understanding that much that other people would have you read is not worth while for you.

True culture has a wide horizon. It is an escape from our own little cell of the space-time continuum. It concerns the attainment of an eminence from which we may survey the intellectual achievements of the human race in our own time and in former times. This demands historical perspective. We glimpse our savage ancestors, clothed in skins, in the distant Age of Stone. We see the early beginnings of agriculture, then of architecture. We hear the crack of slave drivers' whips at the building of the Pyramids. We catch the flash of Phoenician oars on voyages beyond the Pillars of Hercules, venturing thousands of miles to secure amber, tin, and mercury in exchange for glass, niter, papyrus, and Tyrian purple, the products of the chemical industries of that day. We see Roman armies on the march, see Rome overwhelmed by the barbarians, and note how slowly civilization recovered from that blow and how late in the story of mankind were the beginnings of science. Then comes the scientific age, the world transformed by a new mode of thought!

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wandered in our reading and meditation the more illustrations we may command.

A lecture on wrought iron may be made vivid by a quotation from Ferguson's "Forging of the Anchor." Asbestos may recall the travels of Marco Polo. Silk may remind us of its introduction into the Roman world, in the time of Justinian, through cocoons hidden in the walking-staves of traveling monks. Paper may appear as an item in a sequence leading from clay tablets to papyrus rolls, vellum books, and wood pulp magazines. Copper may lead us to mention Pliny's description of mining operations in a world that possessed slaves but no dynamite. Or a passage in Scott's "Talisman" may come to mind, in which King Richard's broadsword, in a friendly contest, cut through an iron bar; and then in answer the Soldan drew his scimitar, cast a silken scarf into the air, and at one stroke cleft it asunder. In this we see the quality called hardness in contrast with that called temper. To find a wealth of such illustrations the teacher of chemistry need only be alert to the manifold contacts of chemistry, not merely with the practical arts but with history, biography, economics, and imaginative literature.

Now some specific recommendations may be made with regard to the cultural possibilities that are to be found where chemistry borders on other sciences. As chemists you will need to know much of physics. The developments classed as modern physics, since the beginning of the present century, have transformed their science and ours. As cultured men and women in the field of science you should be alert to the things that are implied by the quantum and relativity theories, the general plan of atomic structure, the statistical basis of thermodynamics, the general course of events in radioactive disintegration. These things are constantly leading to important applications in the field of chemistry. Now chemical analyses are made by determinations of the magnetic moment of molecules and by photographing Raman spectra. Atomic weights are now most accurately determined by the mass spectrograph, rather than by classical chemical methods. The time is near at hand when all the details of valence will be explained by studies in the physics of the electronic structure of atoms. If we neglect current progress in physics we shall not only miss cultural possibilities of first importance but shall be unable to understand properly some developments that will become common practice in chemistry within the next ten years.

We should not miss knowing something about the fascinating discoveries that are being made where chemistry meets astronomy. We have probably found out just where the energy comes from that is radiated by the sun and stars. The general course of stellar evolution is now fairly clear. We know something, too, of the principles that have determined the distribution of the stars in space. It is the result of the very laws with which colloidal chemists are familiar in the Brownian movement. The spectra of the stars bear witness that the primitive elements, from which all others probably have developed, are hydrogen and helium. Astronomy gives us a hint of what chemistry would be like at temperatures of tens of thousands of degrees and pressures of millions of atmospheres. Thus we get a broader view of our own science.

You will find cultural inspiration in work that is now being done on the mechanism of heredity. Whether one grows up to be a palm tree or a human being, a blacksmith or a prima donna, a winner of a Nobel prize or just an ordinary chemist is perhaps determined by the chemical configuration of a few molecules within the germ cell. It is inspiring, too, to learn what biochemistry is accomplishing in the development of cellular tissue in test tubes, or in the control of sex, fertility and personality by hormones, or in efforts to synthesize the vitamins. We are approaching the disclosure of some of the most intimate secrets of the universe of living things.

I might point out the broadening influence that a chemist may find in the inter-relationship of his science with geology and meteorology. This would only illustrate further that chemistry in its contacts with other sciences offers opportunity for broadening one's horizon, stimulating one's imagination, deepening one's sympathy, heightening one's appreciation of the fine and beautiful. You will realize that this universe of ours is a universe of law and of harmony, which comes more and more to resemble a great thought as we come to understand it better. Surely this is cultural.

Now we ought to remark that culture should aim at something more than personal satisfaction that one may find in being able to understand something of everything that is happening, on all the frontiers of science. Unfortunately, one may be widely read, yet utterly useless. Humanity still faces too many problems to endure the dilettante. One's effort toward the realization of the capacities that we have called culture should make one better fitted to deal with the problems of his own life and should enable him to take an intelligent interest or an active part in the solution of the problems of the race. We have plenty of these: the problem of overpopulation, the problem of the unfit, the problem of war, the problem of disease, the problem of the conservation of natural resources, the problem of distribution of wealth, the problem of the use of leisure. Civilization must solve these problems or perish, and scientists must lead the way.

One thoroughly schooled in scientific matters will appreciate the value of the scientific method but will realize its limitations. Science is but a feeble means for motivating human life. It enlightens men, but fails to rouse them to deeds of heroism, self-sacrifice, and devotion. It creates wealth, but fails to touch the hearts of those who are most successful in gathering wealth together. It dispels ignorance, but it never launched a crusade. It gives aid in our struggles with the hard surroundings of life, but does not inform us to what end we struggle, or whether the struggle is worth while.

Scientific intelligence employs a tool, the scientific method, to create systematized scientific knowledge. This in turn gives rise to scientific invention. But human welfare demands that scientific intelligence shall be supplemented by moral intelligence, which shall direct the forces of science toward idealistic ends, and philosophical intelligence, which shall consider what those ends ought to be. Yet, intelligence can do little more than direct. A gust of emotion is needed to rouse men to action. Whether we like it or not, armies are set afoot, thrones overturned, social systems shattered, and reforms brought into being, not by all the weighty facts of science, but by the kindling flame of emotion.

The moral and philosophical intelligence of the world would like to bring the energizing emotions of humanity under control. At present it can only mold public opinion by the slow pressure of established facts. Yet it is wise enough and tolerant enough to make use of the help that comes its way, from scientific and mystic sources alike. This is the opportunity for religion. Indeed, a sense of reverence and awe that is akin to the spirit of religion is sure to enter the breast of one who has devoted his life to the study of nature. For science has revealed impressive law and order in all things from the atom to the furthermost spiral nebula; and the same great principles are manifested by the solid rocks beneath our feet, the marvels of chemical change, the wonderful world of living things with which we are surrounded, and the messages that the starlight brings from distant space and remote time.

PRODUCTION OF CHEMICAL DRAWINGS BY A RAPID METHOD

EUGENE W. BLANK

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CONSIDERABLE labor is entailed in the production of numerous, different chemical drawings of apparatus setups. A method of procedure by which the amount of work could be decreased would be of definite value. A method which has proved helpful will be briefly described.

Draw standard pieces of apparatus with India ink on small sections of thin, white Bristol board or a good grade of heavy, bond paper, making the lines rather heavy. Points of contact of the different pieces of apparatus with other pieces should be drawn to the edge of the card. In the figure dotted lines indicate the edges of the small cards on which the drawings have been made and illustrate how the drawings should be arranged. A plentiful supply of drawings representing glass tubing bent to various curves should be available. Stoppers and clamps are best cut to shape from black paper. Rubber connections on glass tubing are indicated by black paper rectangles.

The figure illustrates a distillation setup. A large, white Bristol card is used as a background. On this are arranged the various small cards representing individual pieces of apparatus until the entire setup has been constructed. Cover the arrangement with a sheet of glass to prevent shifting of the cards and photograph the drawing. Any number of variety of drawings can be quickly constructed in this manner and photographed.

Tubing and thermometers are drawn on slender strips of the cardboard and inserted to the proper depth in the necks of flasks or other pieces of apparatus. A stopper is cut from black paper to fit the neck of the flask and laid over the tubing or thermometer in the proper position.

Contents of flasks are represented by half circles cut to fit the flasks on which lines have been drawn indicating the nature of the material.

Block letters can be arranged, on the drawings, as a title, or a caption may be hand printed or typed on a separate sheet of white paper and arranged on the background before photographing.

Make the drawings somewhat large to facilitate the work. Very intricate designs can be kept in order by attaching the small cards to the background with the aid of stamp hinges or mending tissue. Stamp hinges are preferable because they can be removed easily, thus preventing damage to the drawings. The edges of the small cards do not photograph if the drawing is well illuminated from all sides and a correctly timed exposure is made.

FIGURE.—ILLUSTRATING THE MANNER IN WHICH CHEMICAL DRAWINGS CAN BE RAPIDLY BUILT UP BY THE USE OF INDIVIDUAL DRAWINGS OF VARIOUS PIECES OF APPARATUS

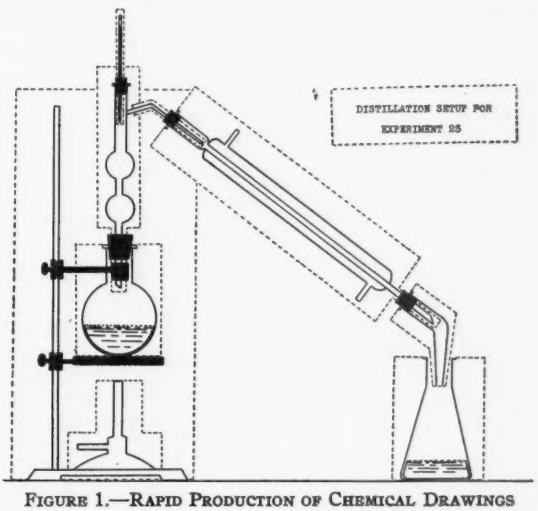


FIGURE 1.—RAPID PRODUCTION OF CHEMICAL DRAWINGS

The CHEMISTRY *of* STOCK-POISONING PLANTS*

JAMES FITTON COUCH

Pathological Division, Bureau of Animal Industry, Washington, D. C.

THE HISTORY of plant poisoning in this country goes back to the time of the earliest settlements. There is record of an outbreak of poisoning in the early days of the Jamestown colony, detailed by Captain John Smith (*106*) in which many of the settlers were made sick by eating of the leaves of the Jimson or Jamestown weed, *Datura stramonium*, under the impression that they would make an agreeable salad. Smith also discovered that perennial public enemy, poison ivy, of which he speaks feelingly. Systematic study of the poisonous plant situation was undertaken by the Department of Agriculture about forty years ago under the leadership of V. K. Chesnut, whose work on the principal poisonous plants of the United States (*13*) is still authoritative. These studies have been continued and extended by several men, notably by Dr. C. Dwight Marsh and by A. B. Clawson who is now in charge of the general project. Much of the information that I shall present was collected by these men, to whom full credit is due.

Poisonous plants may be grouped in a number of ways. They may be classified according to their botanical relationships as monocotyledons or dicotyledons, composites or legumes, or they may be arranged according to the type of physiological effect which they produce as neurotoxins, irritants, depressants, convulsants, and so on. They may be classified according to their habit as shrubs, herbs, or trees, annuals, biennials or perennials, or they may even be arranged in alphabetical order. Since we are primarily interested in the chemical relationships of these organisms, I have adopted a classification of the poisonous plants based upon the chemical groups into which their active principles naturally fall. By this method plants are divided into the following categories: the alkaloidal, glucosidal, including the cyanogenetic and saponinic, the phytotoxin, resinoid, oxalic acid, and phenolic, with a miscellaneous group into which are placed those plants whose active principles are unique in chemical characters and do not fall into any other convenient classification.

The number of plants that contain toxic substances, and so are potentially poisonous, is very large and any sufficient discussion of all of them would require much more space than is at my disposal. I shall, therefore, confine this discussion to the more important poisonous plants with particular reference to those that cause notable losses of livestock in the United States. The importance of these plants may be realized when it is understood that the annual losses of livestock due to plant poisoning are estimated to exceed $2,000,000 and in some years may be much larger. In one extensive outbreak in Texas it was estimated that during one spring alone animals valued at $300,000 died from the effects of one plant species. Single losses involving five to ten thousand dollars are not uncommon, while losses involving smaller amounts occur continually over the length and breadth of the country. In Oregon last spring losses exceeded $40,000, of which amount $25,000 was sustained by one company. A large part of the loss due to stock poisoning is preventable and calls for little more than recognition of the dangerous plants and reasonable care in pasturing animals.

In spite of a widespread belief that animals are protected by some kind of instinct that warns them against eating such plants, livestock will graze sometimes on very dangerous plants when plenty of good feed is available. It is true that many of the poisonous plants are unpalatable to animals and will be eaten only when the animals are driven to it by hunger, but this is not always the case. One cannot, therefore, rely on some instinctive reaction of the animal for protection from this danger. On the other hand, well-fed animals are reasonably safe in the majority of cases. In one instance in our experience a certain livestock breeder in Montana had pastured his animals for years in a locality where two very poisonous species of plants, white loco weed and death camas, were abundant, and yet he had not lost any animals and was surprised to learn that these plants are regarded as very dangerous. His escape from the usual consequences of this situation was due to the fact that he never overgrazed his pastures, but always had plenty of good feed for his herds which were, as a result, never hungry enough to feed on the poisonous species.

THE ALKALOIDAL PLANTS

All plants contain basic nitrogenous substances, protein degradation products, choline, betaine, or similar compounds that will react with alkaloidal reagents, but the occurrence of alkaloids in the accepted use of that somewhat indefinite term is confined to a rather restricted number of botanical groups. Some of the large groups of plants do not so metabolize their nitrogen as to yield alkaloids. This is true of the very large family of labiates that includes the mints and their relatives and is also generally true of the composites, although in this case there is one outstanding exception in the *Senecios*. The grasses are not characteristically alkaloid-bearing, although *Lolium temulentum* (darnel)

* Adapted from the Address of the retiring president, Chemical Society of Washington, January 9, 1936.

yields loliine, a true base. The palms, with the exception of the areca or betel palm, are non-alkaloidal. These bases are yielded customarily by such important families as the legumes, the ranunculaceæ, the solanums, the papveraceæ, and others among the dicotyledons and by the lilies and amaryllises, notably among the monocots.

Larkspur, Delphinium species.—Of the alkaloidal plants the most important are the larkspurs (Figures 1 and 2), a genus of ranunculaceæ, which is widely distributed in the United States. Marsh, Clawson, and Marsh (*79*) list twenty-six possibly poisonous species.

FIGURE 1.—TALL LARKSPUR, *Delphinium barbeyi*

In the Appalachian district a species known as *Delphinium tricorne* is distinctly poisonous, and the genus is represented on the great plains and in the Rocky Mountains by other species which annually exact a heavy toll from livestock breeders (*53*). The chemistry of the larkspurs is in a very unsatisfactory state. We have some quite definite knowledge of the alkaloids of certain European species, *D. ajacis*, *D. consolida* (*70*), and *D. staphisagria* (*71*), but very little has been published about the American plants, and what is available in this respect usually is little more than a figure for the content of alkaloids without any information concerning their chemical identity. Thirty years ago Heyl (*54*) reported the isolation of an alkaloid, which he named delphocurarine, from larkspurs growing in Wyoming, and recently a study of another species, *D. occidentale*, has been taken up in our laboratory with encouraging results.*

* Since the above was written the account of the isolation of a new alkaloid from this plant has been published, J. F. COUCH, *J. Am. Chem. Soc.*, **58**, 684–5 (1936).

Spontaneous larkspur poisoning is observed principally in cattle. Horses and sheep may also be poisoned under exceptional conditions. The symptoms observed are weakness, depression, trembling, and constipation, with death from respiratory paralysis. The poisoning is acute and the toxic alkaloids appear to be rapidly eliminated through the kidneys. Chronic cases have not been observed.

FIGURE 2.—LOW LARKSPUR, *Delphinium menziesii*

FIGURE 3.—LUPINE, *Lupinus inyoensis*

Lupines.—Lupines (Figure 3) are important stock-poisoning plants on the ranges of the western states and Pacific coast. The genus *Lupinus* includes about one hundred fifty different species, of which some are

very poisonous, others cause poisoning only under special circumstances, and still others appear to be innocuous under range conditions. As legumes the lupines are potentially valuable forage plants and when they are not dangerous furnish very good feed for grazing herds. A great deal of chemical work has been done on the lupine alkaloids with very interesting results. About seventy-five years ago, stimulated by a series of wholesale poisonings of sheep in Germany, there were initiated intensive studies of the European species. After thirty years of effort on the part of a number of investigators (Baumert (*4*), Schmidt (*104*), Davis (*36*), Willstätter (*117*)) we had obtained fairly complete information concerning the chemistry of four species, *Lupinus albus*, *L. angustifolius*, *L. polyphyllus*, *L. luteus* and its sport called *L. niger*. These contain the following alkaloids: sparteine, lupinine, *d*-lupanine, *dl*-lupanine, and hydroxylupanine. The third and fifth were found in *L. polyphyllus*, an American species often grown in Europe as an ornamental. Aside from this case nothing was known of the identity of the alkaloids in the American lupines twenty years ago. Since that time some thirty species of American lupines have been examined with the result that a large number of new alkaloids has been isolated, and in addition, except for *dl*-lupanine, the remainder of the European alkaloids has been discovered in American lupines.

TABLE 1

LUPINE SPECIES AND THEIR ALKALOIDS

Lupinus	*Alkaloids*	*Authority*
luteus	sparteine and lupinine	Willstätter and Fourneau (*117*)
niger	sparteine and lupinine	Gerhard (*45*)
angustifolius	*d*-lupanine	Hagan (*48*)
albus	*d*-lupanine and *dl*-lupanine	Davis (*36*)
polyphyllus	*d*-lupanine and hydroxylupanine	Bergh (*7*)
leucopsis	leucopsine	Black (*8*)
argenteus	unnamed	Beath (*5*)
sericeus	unnamed	Sollmann (*107*)
leucophyllus	unnamed	Sollmann (*107*)
termis	*dl*-lupanine	Clemo and Leitch (*19*)
arboreus	sparteine	Jaretzky and Axer (*60*)
barkeri	sparteine	Jaretzky and Axer (*60*)
elegans	sparteine	Jaretzky and Axer (*60*)
barbiger	sparteine, dilupine, trilupine	Couch (*20*)
spathulatus	spathulatine	Couch (*21*)
kingii	*d*-lupanine	Couch (*22*)
corymbosus	hexalupine and heptalupine	Couch (*23*)
caudatus	monolupine	Couch (*24*)
palmeri	lupinine, tetralupine, and pentalupine	Couch (*25*)

TABLE 2

LUPINE ALKALOIDS OCCURRING IN MORE THAN ONE SPECIES

Sparteine: *Lupinus luteus, L. barbiger, L. arboreus, L. barkeri, L. elegans.*
Lupinine: *Lupinus luteus, L. palmeri.*
d-Lupanine: *Lupinus albus, L. angustifolius, L. polyphyllus, L. kingii.*
dl-Lupanine: *Lupinus albus, L. termis.*

The lupine alkaloids act upon the central nervous system to depress the motor functions. There are differences in the symptoms shown by animals poisoned by different species. Sheep on some lupines exhibit a train of symptoms indicative of nervous stimulation; on other lupines the symptoms are those of depression only. Cattle and horses are depressed. In this country acute poisoning alone has been observed but in Germany a chronic condition known as lupinoisis (*1*) was at one time very prevalent. This has been shown to be due to moldy lupines in which there develops a protein-like toxin, ictrogen (*1*), not present in the unmolded plant.

Senecios.—The genus *Senecio*, the groundsels (Figure 4) is the single representative of the composite family that is important because of its alkaloidal content. In recent years it has been found (*17*, *113*) that species of this genus are responsible for certain hitherto obscure intoxications that had been attributed to other plants.

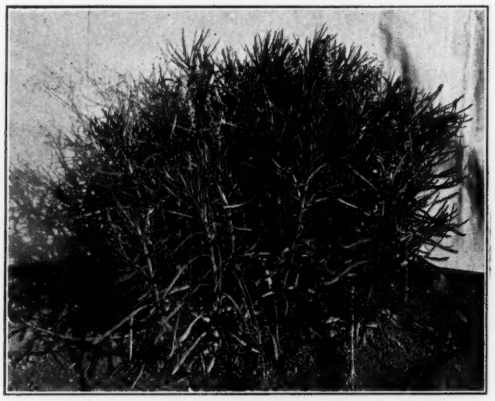


FIGURE 4.—GROUNDSEL, *Senecio spartioides*

A number of species has been investigated in several parts of the world. In South Africa where *Senecio* species are credited with causing many losses, ten toxic species are listed by Steyn (*108*), of which chemical information is available concerning three. Manske (*64*) found in *Senecio retrorsus*, retrorsine, $C_{16}H_{25}NO_6$; Grandval and Lajoux (*47*) isolated senecionine, $C_{18}H_{25}NO_6$, and senecine from *S. vulgaria*, and H. E. Watt (*115*) reported senecifoline, $C_{18}H_{27}NO_8$, and senecifolidine, $C_{18}H_{25}NO_6$, from *S. latifolius*, all from South Africa. Manske (*64*) isolated jacobine, $C_{18}H_{23}NO_5$, from *S. jacobæa*. Orechoff (*91*, *92*) has obtained platyphylline, $C_{18}H_{25}NO_5$, and seneciphylline, $C_{17}H_{23}NO_5$, from *S. platyphyllus*, native in the Caucasus. Of the American species that have been shown to cause serious poisoning of livestock, *S. riddellii* (*113*), *S. longilobus*, *S. integerrimus*, and *S. spartioides* (*17*), nothing is known with respect to their chemical constituents. It is interesting that, unlike most alkaloidal intoxications, these plants cause a chronic disease called "seneciosis," which is characterized by (among other things) lesions in the liver, technically termed parenchymatous hepatitis.

Other alkaloidal plants.—The spotted hemlock (*Conium maculatum*) occasionally causes poisoning and contains the very toxic alkaloid coniine, $C_8H_{17}N$, *d*-propylpiperidine, noted as the lethal constituent of the draught used by the ancient Greeks in executing criminals. Cases of poisoning are occasionally caused by the solanaceous plants, Jimson weed, *Datura stramonium*, which contains hyoscyamine or hyoscine, and henbane (*Hyoscyamus niger*), which contains hyoscy-

amine, atropine, atrocine, and hyoscine. Boxwood (*Buxus sempervirens*) yields buxine or bebeerine $C_{18}H_{21}NO_4$ (*44*). False indigo (*Baptisia tinctoria*) yields cytisine, $C_{11}H_{14}N_2O$, which occurs in a large number of plants and in the Baptisia is reinforced by a poisonous glucoside, baptisin, $C_{26}H_{32}O_{14}$ (6% of root) (*46*). Animals will sometimes feed on wild tobacco with fatal results. Two species of this genus have been investigated; *Nicotiana trigonophylla* was found by Black (*9*) to contain 0.39% of nicotine and another wild species, *Nicotiana attenuata* (*26*) (Figure 5), was found to contain 1.45% of that alkaloid in the dry leaves.

An important group of poisonous plants, the death camas (*Zygadenus*, Figure 6), also owes its toxic properties to alkaloids. The death camas, so named because it has been mistaken for the edible camas (*Quamasia quamash*), constitutes a serious menace to the sheep industry (*75*). Little can be stated about the alkaloids of this group beyond the fact that they appear to be related to veratrine. The alkaloid, zygadenine, $C_{39}H_{63}NO_{10}$, was isolated by Heyl and Raiford (*51*). Heyl,

FIGURE 5.—WILD TOBACCO, *Nicotiana attenuata*

FIGURE 6.—DEATH CAMAS, *Zygadenus elegans*

FIGURE 7.—DUTCHMAN'S BREECHES, *Dicentra cucullaria*

Knight, Loy, and Prien (*52*) separated basic fractions from *Zygadenus intermedius*, which they demonstrated to cause the characteristic effects of the plant when administered to animals. Slade (*105*) obtained similar fractions from *Z. venenosus*. Little or nothing is known about the identity of the alkaloids of other important species, *Z. gramineus*, *Z. paniculatus*, and *Z. elegans*.

Other alkaloidal plants that occasionally cause poisoning of livestock but are of smaller importance are: coral bean, *Sophora secundiflora*, which contains the very toxic alkaloid cytisine (*95*). This plant has been reported as the cause of poisoning in Texas (*11*). *Peganum harmala* has recently been reported as an immigrant in New Mexico (*88*). This plant contains toxic alkaloids (*93*), and if it continues to spread may become a serious menace to the cattle industry in that state. Very interesting data are being collected about species of *Dicentra* (*Bikukulla*) (Figure 7), a genus of the *Papaveraceæ*. A number of these toxic species have been studied, principally by Manske, and the nature of the alkaloids determined. The data are presented in Table 3.

The crotalarias or rattle-boxes have been recognized as poisonous for many years (*100*). At one time it was thought that the symptoms of loco disease were due to *Crotalaria sagittalis*, from which Power and Cambier obtained an alkaloid (*98*). Recently Neal, Rusoff, and Ahman (*89*) obtained a new toxic alkaloid, monocrotaline, from *C. spectabilis*, poisonous to livestock in the southern states. Reference may also be made to jasmine, *Gelsemium sempervirens*, which contains the toxic alkaloid gelsemine, $C_{20}H_{22}N_2O_2$ (*85*), and the less toxic gelseminine which may be a mixture of bases.

TABLE 3

ALKALOIDS IN SPECIES OF *Dicentra* (*Bikukulla*)

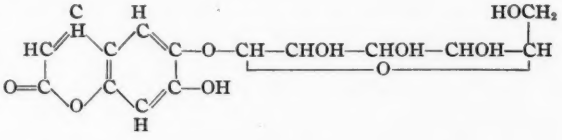
Species	*Alkaloids*	*Authority*
D. cucullaria	Protopine, cryptopine, bicuculline, cucullarine	Manske (*66*) Black, *et al.* (*10*)
D. canadensis	Protopine, bulbocapnine, corydine, isocorydine	Manske (*65*)
D. spectabilis	Protopine	Danckwortt (*35*)
D. Formosa	Protopine, dicentrine, glaucine, corytuberine, corydine	Manske (*68*) Black, *et al.* (*10*)
D. pusilla	Protopine, dicentrine	Asahina (*2*)
D. oregana	Protopine, glaucine, corydine, dicentrine, α-allocryptopine	Manske (*69*)
D. eximia	Protopine, *d*-glaucine, eximine, eximidine, isocorydine, dicentrine	Manske (*67*)

GLUCOSIDAL PLANTS

Glucosides are substances which, on hydrolysis, yield a sugar and a non-carbohydrate fragment known as aglycone. They are widely distributed in nature, and many of them are highly toxic. They are divided into subgroups according to the character of the sugar and also according to the character of the aglycone. Because of their importance in toxicology especial mention may be made of the phenol glucosides, the cyanogenetic glucosides, and the saponins.

Glucosides are substances notoriously difficult to isolate from plant material. They differ widely in their solubilities, and because of their tendencies to hydrolyze require skilful treatment. There is no procedure generally applicable to their isolation and purification; the methods used must be adapted to the case in hand, and differ considerably with different members of the group.

Buckeye.—The Ohio buckeye, *Aesculus pavia*, and related species have been the source of sporadic losses of livestock for more than a century. The toxic properties are referred to aesculin, $C_{15}H_{16}O_9 \cdot 2H_2O$, m. p. 205° (*119*), which, on hydrolysis with dilute acids or emulsin, yields dextrose and æsculetin, or 6,7-dihydroxycoumarin, $C_9H_6O_4$ (m. p. 268°). Æsculin is, therefore, 6-glucosidoæsculetin (*62*).



Hemp.—Indian hemp (*Apocynum cannabinum* (Figure 8)) contains at least one toxic glucoside, cymarin

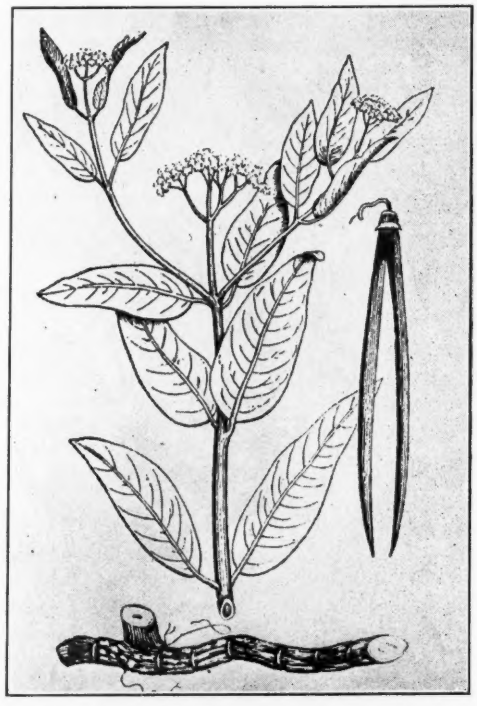


FIGURE 8.—INDIAN HEMP, *Apocynum cannabinum*

(*56*), in addition to a poisonous resin that is apparently non-glucosidic (*103*). Three other toxins have been reported (*103*): a glucoside, apocynein; a resin, apocynin, later identified as acetovanillon (*40*); and cynotoxin, $C_{20}H_{38}O_6$.

Cymarin hydrolyzes to cynamarigenin, $C_{23}H_{30}O_6$, and a heptose, cymarose, $C_7H_{14}O_4$.

The closely related species, dogbane, *Apocynum androsaemifolium*, has been the subject of several chemical studies, but there still remains some uncertainty as to the character of the active principles. Moore (*87*) attributed its action to apocynamarin, $C_{14}H_{18}O_3$, a bitter principle, which Impens (*56*) considers a decomposition product of the true toxin. Apocynamarin is possibly identical with cynamarigenin, and if this is confirmed the toxic agent in *A. androsaemifolium* is the same or closely related to cynamarin.

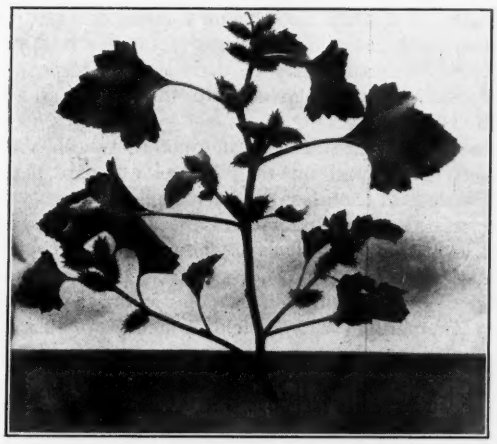


FIGURE 9.—COCKLEBUR, *Xanthium* sp.

Cockleburs.—Cockleburs (Figure 9), species of *Xanthium*, are a perennial source of fatal poisoning to livestock (*82*), and particularly to pigs. These plants contain a poisonous glucoside, xanthostrumarin (*118*), which is stored in the seed. When the seed germinates the poison appears in the cotyledons and earliest leaves and at this stage of growth the plant is very toxic. As the plant matures its dangerous nature disappears and the adult plant appears incapable of causing poisoning.

FIGURE 10.—ARROWGRASS, *Triglochin maritima*

Other glucosidal plants.—Among other glucoside-bearing plants may be mentioned western sneezeweed, *Helenium hoopesii*, which causes a chronic spewing disease in sheep and cattle (*78*), and foxglove (*Digitalis purpurea*) which, while not native, escapes from cultivation and occasionally causes losses. Several species of milkweeds, *Asclepias galioides*, *A. mexicana*, *A. pumila*, and *A. verticillata*, contain very active glucosides (*77*), the chemistry of which remains to be worked out.

CYANOGENETIC PLANTS

One of the most important groups of glucoside-bearing stock-poisoning plants is that whose members have the property of evolving or developing hydrocyanic acid under suitable conditions. Species of this type are to be found almost everywhere in the United States and are widely distributed in other parts of the world as well. In every case where the chemistry is clearly understood the mechanism of the evolution of hydrocyanic acid has been found to be the action of an emulsin-type enzyme upon a nitrile glucoside. The principal cyanogenetic plants in the United States (*27*) include arrow grass, *Triglochin maritima* (Figure 10) (*81*, *42*); sorghum, *Sorghum vulgare;* Johnson grass, *Sorghum halepense;* Sudan grass, *Sorghum vulgare sudanense;* flax, *Linum usitatissimum;* and the wild cherries, *Prunus virginiana*, *P. serotina* *P. melanocarpa*, *P. demissa* (*84*), and possibly other species. The sorghums contain dhurrin, $C_{14}H_{17}NO_7$, which hydrolyzes to *p*-hydroxybenzaldehyde, glucose, and hydrocyanic acid (*37*). Flax yields linamarin (*38*), $C_{10}H_7NO_3$, also found in certain varieties of wild lima beans (*Phaseolus lunatus*), whence the alternative name phaseolunatin. This glucoside hydrolyzes to acetone, glucose, and hydrocyanic acid. The cherries yield amygdalin or similar glucosides which hydrolyze under the influence of enzymes to benzaldehyde, glucose, and hydrocyanic acid (*97*). The cyanogenetic compound in arrow grass has not yet been isolated but there is no good reason to think that it departs very far from the general type.

The symptoms exhibited by animals poisoned by cyanogenetic plants are the same as are seen in cases of cyanide poisoning. There is a preliminary stimulation of the respiration, rapidly changing to dyspnea, paralysis of the voluntary muscles with staggering, collapse, spasms, complete loss of consciousness, cyanosis of the visible mucous membranes, and death from asphyxiation after a variable period of illness, usually short, but occasionally prolonged. One of the earliest reports of the danger of cyanogenetic plants to livestock in the United States was published by Peters, Slade, and Avery (*94*) thirty years ago. Since that time the subject has been investigated by a number of workers and a large amount of information is available. Reference may be made especially to the publications of Marsh and Clawson (*81*) and Fleming *et al.* (*42*) on arrow grass; of Flemming, Miller, and Vawter (*43*) on *Prunus demissa;* of H. N. Vinall (*114*), Peters, Slade and Avery, Paul Menaul and C. T. Dowell (*83*), and Dunstan and Henry on sorghum poisoning.

Although hydrocyanic acid is a very rapidly acting poison and so offers little opportunity for the action of remedies, recent work has demonstrated that, if the victim can be reached in time, sodium thiosulfate and sodium nitrite given intraperitoneally or intravenously

are effective antidotes against rather large doses. A large number of reports has been issued during the past four years bearing on the use of these remedies, either singly or in combination, against cyanide poisoning in a variety of kinds of animals. The effectiveness of the antidotal treatment in the case of sheep and cattle has been investigated by Clawson, Bunyea, and Couch (*18*),* who have demonstrated that, if given within a short time after the animal shows symptoms of poisoning, the remedy is effective against as high as three minimal lethal doses.

THE SAPONIN PLANTS

A large group of poisonous plants owe their toxic properties to the presence of saponins which differ from other glucosides in that they are usually non-crystalline, insoluble in concentrated alcohol, but soluble in water, forming solutions that foam persistently like soap solutions. Many, probably most, of the saponins

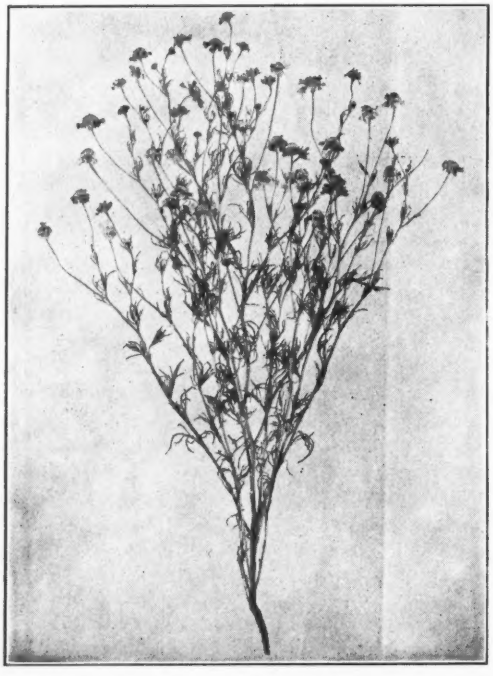


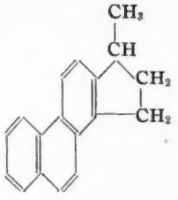
FIGURE 11.—BITTER RUBBERWEED, *Actinea odorata*

are harmless when taken by mouth, but some very toxic members of this class are known. These act not only through their hemolytic powers but also by a directly depressant action upon the central nervous system, and some cause local lesions in the liver and other parenchymatous organs.

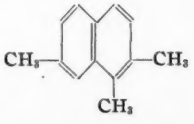
The saponins are widely distributed in nature. Among the poisonous plants they are especially important in such groups as the composites, caryophyllaceæ, and scrophulariaceæ, as well as in others that are not represented in the United States by poisonous species.

Chemically they are complex glucosides that, on hydrolysis, yield sugars and aglycones known as sapogenins. Because of the difficulty of preparing these substances in pure condition due to their tendency to adsorb salts from solutions, the chemistry of the saponins was much confused during the past century. Recent attacks on the problem by van der Haar, Ruzicka, Windaus, and others have begun to bring order into the confusion of data. From these researches it appears that the sapogenins may be derived from terpene-like predecessors and are related to the sterols and bile acids.

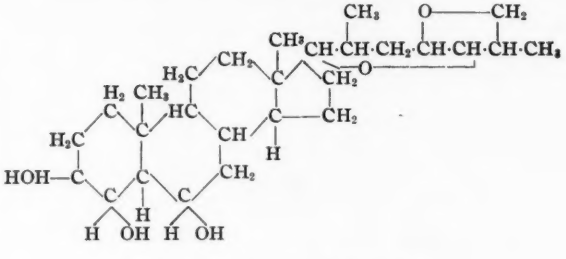
The former classification of saponins established by Kobert (*61*), based on their behavior toward neutral and basic lead acetates, has been replaced by a system that refers to the character of the aglycone or genin, formed in their hydrolysis as determined by the selenium dehydrogenation process (*110*). The first group, typified by the digitalis saponins and by parillin from sarsaparilla (*57*, *58*), yields 1-methylcyclopentenophenanthrene:



The second group, typified by cyclamin, $C_{63}H_{112}O_{33}$, and aescin, $C_{53}H_{85}O_{27}$, yield sapotalin or 1,2,7-trimethylnaphthalene,



Some idea of the complexity of the saponins may be gained from the fact that digitonin, $C_{56}H_{92}O_{29}$, when hydrolyzed breaks into four molecules of dextrose, one of xylose and one of digitogenin, $C_{27}H_{44}O_5$, for which the indicated structure has been suggested (*111*).



Suggested structure of digitonin.

* For a general statement of the results see BUNYEA, H., *J. Am. Vet. Med. Assoc.*, **86**, 656–61 (1935).

Results obtained by Ruzicka and his co-workers (*101*) indicate that the skeleton of the second group of sapogenins is a trimethylpicene. The relationships between the saponins and the sterols, bile acids (*111*), sexual hormones, and carcinogenic compounds is one of the most provocative developments of recent chemical research (*112*).

As representative of the saponin plants may be mentioned two species of *Actinea*. Pingue (*Actinea richardsoni*) or rubber weed, so called because it contains 3–5% of caoutchouc, causes a good deal of trouble to sheep raisers in some of the Western States because of its poisonous properties. The related bitter rubber weed (*A. odorata*) (Figure 11), or Texas bitterweed, has invaded large sections of range land in the Southwest and under favorable conditions causes large losses, especially in sheep and goats. Both plants contain saponins and their toxicity is apparently due to these glucosides. Ordinarily the poisoning is chronic rather than acute and is characterized by weakness, depression, vomiting, and death (*15*).

Corn cockle, *Agrostemma githago*, is a troublesome weed, the seeds of which contain very toxic saponins (*102*), named githagin by early investigators. Wedekind and Krecke (*116*) studied the hydrolytic products of this mixture and obtained the aglycone, githagenin, $C_{28}H_{44}O_4$, and glucuronic acid, or an isomer.

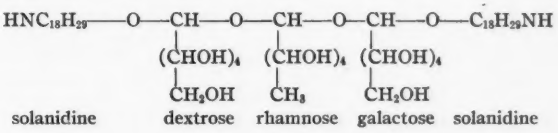
SOLANINE PLANTS

A number of solanaceous plants owe their toxic characters to the presence of a complex substance, solanine, which is at once alkaloidal and saponinic, in that, while it contains basic nitrogen and behaves like an alkaloid, it also behaves like a saponin and may be hydrolyzed to yield a basic aglycone, solanidine, and a mixture of sugars, dextrose, rhamnose, and galactose (*90*). Recent investigations indicate that there may be solanines differing in composition and in the nature of the aglycone formed on hydrolysis. But the different bodies agree in their general chemical, physical, and physiological characters.

FIGURE 12.—BULL NETTLE, *Solanum carolinense*

Occasional poisoning due to eating sprouted potatoes or the leaves and stems of the potato plant is referable to the presence of solanine in these tissues. Heiduschka and Sieger (*50*) report for solanine from potatoes the formula $C_{52}H_{91}NO_{18}$, and for its aglycone, solanidine, $C_{34}H_{57}NO_2$.

To solanine S, from *Solanum sodomeum*, $C_{54}H_{96}N_2O_{18}$, the following partial constitution has been assigned (*90*):



The toxic effects of the native American species, *Solanum carolinense* (bull nettle) (Figure 12), *S. dulcamara* (Bittersweet), and, doubtfully, *S. nigrum* are attributed to solanine. Another solanine has been isolated from the herbaceous parts of the common tomato plant.

PHYTOTOXINS

A few plants contain poisonous substances that belong to the general group of proteins and appear to be true antigens like the bacterial toxins. They have been termed phytotoxins in recognition of this character. Cases of poisoning have been reported from two such plants in this country. The common black locust, *Robinia pseudoacacia*, contains a very active phytotoxin, robin, isolated by F. B. Power (*98*, *99*); and the cultivated castor bean or palma Christi, *Ricinus communis*, contains ricin (*109*), also very poisonous.

RESINOID PLANTS

A very important class of poisons is included under the term resinoid. These are substances which, as the name implies, have the physical characters of resins. They are very difficult to purify, most of them have not been crystallized, and their chemical relationships often remain problematical. Some plants belonging to the heath family, *Ericaceæ*, contain a very poisonous resinoid, andromedotoxin (*96*), formerly known as asebotoxin (*39*). The most recent revision of its chemistry assigns to it the formula $C_{19}H_{32}O_6$ or $C_{19}H_{30}O_6$ (*49*). This substance is widely distributed among the ericaceous plants over the world. In our native plants it is undoubtedly responsible for the poisonous character of *Rhododendron maximum* (Figure 13), *Pieris mariana*, *Leucothoe catesbaei*, *Kalmia latifolia* (Figure 14), *K.*

FIGURE 13.—WHITE-FLOWERED RHODODENDRON, *Rhododendron albiflorum*

angustifolia, *K. microphylla* (*16*), *Leucothoë davisii* (*73*), and species of *Azalea*.

These plants may poison any class of grazing animal. The symptoms observed are salivation, vomiting, and weakness, frequently with a fatal termination (Figure 15). Andromedotoxin is so active a poison that it would be of great interest to know its chemical structure and learn something of the peculiar groupings that cause its physiological properties.

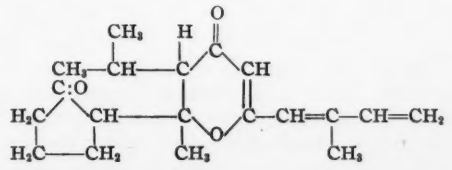
Of special interest is the fact that honey made from flowers of these plants is very poisonous. Apparently the andromedotoxin is taken up by the bees in gathering the honey and deposited in the hive. The outbreak of sickness among the 10,000 Greeks as related by Xenophon in the Anabasis has been attributed by some to this source.

FIGURE 15.—A SHEEP POISONED BY MOUNTAIN LAUREL

FIGURE 14.—MOUNTAIN LAUREL, *Kalmia latifolia*

FIGURE 16.—WATER HEMLOCK, *Cicuta vagans*

Another very active member of this class is the resinoid cicutoxin, $C_{19}H_{26}O_3$, the active principle of the very toxic water hemlock (*Cicuta vagans*) (Figure 16) of the umbellifer family. Jacobson (*59*) has suggested this structure for cicutoxin:



The *Cicutas* are widely distributed and may be found in low swampy places nearly everywhere. Poisoning from them occurs usually in the spring, when the ground is soft and the roots may readily be pulled up from the soil. The symptoms are violent spasms. *Cicuta* is without doubt the most poisonous plant that grows in this country and annually causes large loss of livestock. Children are often tempted to eat the root by its attractive odor, and many fatalities have resulted from this source.

The active agents in at least two of the toxic milkweeds are also to be included in this group. Galitoxin (*77*), the spasmodic toxin of the whorled milkweed (*Asclepias galioides*) (Figure 17), is a resinoid. Analysis of the purest material yet obtained leads to the probable formula $C_{17}H_{24}O_4$. Next to *Cicuta vagans*, this whorled milkweed is one of the most poisonous plants in the United States. As little as three ounces of the fresh plant are sufficient to cause the death of an adult sheep. Symptoms observed are violent spasms and these are also caused by galitoxin (Figure 18). There are also glucosides in the plant, but the action of these substances is masked by the greater activity of the resinoid. Losses from this plant have been severe. In 1918, four hundred sheep died from feeding on this plant near Hotchkiss, Colorado. In 1917, a loss of

FIGURE 18.—A HORSE POISONED BY WHORLED MILKWEED

FIGURE 17.—WHORLED MILKWEED, *Asclepias galioides*

FIGURE 19.—WOOLLY POD MILKWEED, *Asclepias eriocarpa*

seven hundred thirty-six sheep out of a band of one thousand was traced to this cause near Cortez, Colorado, in an area where, over a period of three or four years, $35,000 to $45,000 worth of livestock had been fatally poisoned.

A related species, the woolly pod milkweed (*Asclepias eriocarpa*) (Figure 19), is also very poisonous. This plant does not contain galitoxin but another resinoid which differs from it by being alkali-soluble (*28*). Extensive losses in California have been traced to this plant.

The symptoms exhibited by animals poisoned with Mexican whorled milkweed (*Asclepias mexicana*) (*74*), and the chemical evidence obtained by Miller (*84*) suggest that galitoxin, or a closely related substance, occurs in this plant also.

OXALIC ACID PLANTS

Oxalic acid combined as sodium or potassium oxalate, usually as acid salt, is found in a large number of plants but seldom in quantities sufficient to cause illness. The leaves of the garden rhubarb contain enough of this substance to cause poisoning, however, and occasionally cases of the sort are reported. Wild species of the genera *Rumex* and *Xanthoxalis*, like the sheep sorrel and sour dock, frequently cause poisoning due to their content of this acid (*Rumex acetosella*, *Rumex acetosa*, *Xanthoxalis stricta*, *Oxalis acetosella*). The most important member of this group in this country is greasewood (*Sarcobatus vermiculatus*) (Figure 20) that grows abundantly in the arid regions of the Western

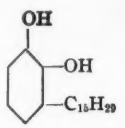
FIGURE 20.—GREASEWOOD, *Sarcobatus vermiculatus*

States (*73*). The air-dried leaves of this plant were found to contain 9.4% of oxalic acid combined mainly as the neutral oxalates of sodium and potassium (*33*, *84a*). When hungry sheep are allowed to feed on this plant, poisoning frequently results. Chesnut and Wilcox (*14*) refer to a loss of one thousand sheep in New Mexico from this plant. In 1920 an outbreak at Harper, Oregon, occurred in which out of a band of seventeen hundred ewes that grazed on a greasewood area one thousand died during the night. Experimental work indicated that 1.5 pounds of the fresh plant fed to an adult sheep in a single feeding would cause death but that, if eaten slowly, much larger quantities, four to eight pounds, could be eaten daily for a prolonged period without harm. Metabolism experiments made on these cases indicated the surprising fact that the sheep is able to metabolize oxalic acid rather rapidly, although other mammals, so far as is known, are unable to do this, and excrete the greater part of the ingested oxalic acid unchanged through the kidneys.

FIGURE 21.—BLUE LOCO, *Astragalus diphysus*

PHENOLIC PLANTS

The most interesting of this group is poison ivy (*Toxicodendron radicans* and its relatives *T. vernix* and *T. diversiloba*). G. A. Hill, V. Mattacotti, and W. D. Graham (*55*) have recently shown that the toxic principle of this plant is the same as that isolated from the Japanese species *Rhus vernicifera*, namely, urushiol (*63*).



Urushiol appears to be a mixture of *o*-dihydroxybenzenes with an adjacent normal pentadecylene group. When the OH was masked by methyl the compound

was non-toxic. It is interesting, in view of the extreme activity of urushiol when in contact with the skin, that the plant is eaten by grazing animals without effect. In animal husbandry it cannot be listed as a poisonous plant.

Other plants that probably depend upon phenolic compounds for what toxic effects they exhibit are the sneezeweed (*Helenium autumnale*), and bitterweed (*Helenium tenuifolium*),* and probably also the spurge, better known as snow-on-the-mountain (*Euphorbia marginata*), which resembles poison ivy in its effects.

THE LOCO WEEDS

The most important group of stock-poisoning plants in the United States is that which comprises the loco weeds. These are species of the genera *Astragalus* and *Oxytropis* which cause a characteristic syndrome called "loco disease," from the Spanish word for crazy. A

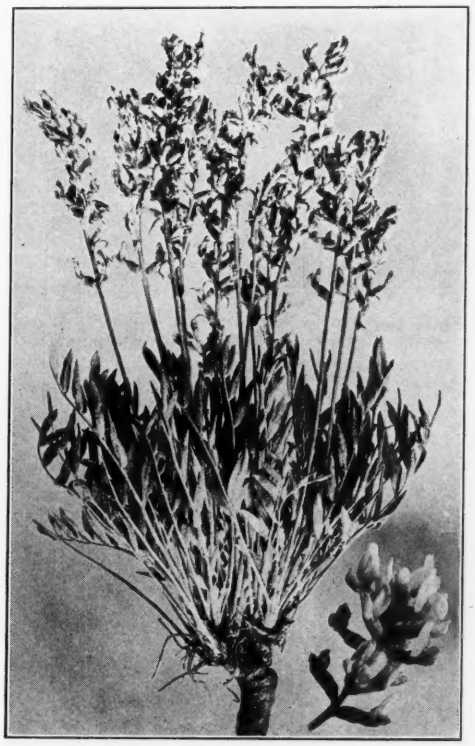


FIGURE 22.—WHITE LOCO, *Oxytropis lambertii*

number of species in these genera are known to cause this peculiar condition, the principal types being *Astragalus mollissimus*, or purple loco, *A. diphysus* (Figure 21), or blue loco, and *Oxytropis lambertii* (Figure 22), or white loco (*72*). The white and purple locos are widely distributed over the Great Plains States and frequently occur in large patches (Figure 23). Losses of horses, cattle, and sheep from locoism have been heavy. In 1883, twenty-five thousand cattle died from this cause in one section of Kansas, and in 1898 breeders in Colorado suffered a loss of $117,300 worth of livestock. The condition was so serious that the state of Colorado expended $450,000 over a period of nine years in an attempt to eradicate the weeds (*3*).

Locoed animals are dull and depressed. The hair is long and staring. Evidence of muscular incoördination is manifested by irregularities in the gait, dragging of the hind feet, and palsied shaking of the head. There are disturbances of vision; the animal may not be able to see clearly men or other objects at a moderate distance and is unable to judge the height of obstacles on the ground so that in stepping over a rope lying on the ground the horse may step high enough to clear two feet or he may jump over a small rut as if it were a sizable ditch. Nervous symptoms are characteristic (Figure 24). The animal becomes timorous, is easily startled, and may shy violently and is difficult to lead or drive. The animal becomes emaciated and eventually very weak, and death finally occurs after a variable period.

The chemistry of the loco weeds has been the subject of many investigations during the past fifty years (*34*) to isolate the particular substance responsible for the symptoms, but complete success has not yet been achieved. The compound has been obtained in a nearly pure but non-crystalline state (*29*). It is a highly hygroscopic powder soluble in water, methanol, and ethanol but quite insoluble in chloroform, ether, and the hydrocarbon solvents. It does not fall into any of the well-known groups of poisons. Analysis indicates C, H, N, and O nearly in the proportions of 19, 35, 2, and 12. The substance is not basic and since it yields pyrrole derivatives on distillation the nitrogen may be combined as an imido group. The large proportion of oxygen suggests that it is highly hydroxylated, but no reducing carbohydrate can be obtained from it. This substance has been obtained from *O. lambertii* and the same or a very closely related compound occurs in *A. diphysus*.

MILK SICKNESS

The cause of this very mysterious disease which was prevalent in the early settlements, principally of the middle west, and resulted in the deaths of many persons as well as the loss of a large number of livestock, remained obscure for more than a century in spite of many earnest attempts to solve the problem. Its history is a record of controversy and wild speculation mingled with doubts and frank terror in the affected population. In order to escape the disease people abandoned farms and villages, and an outbreak was followed by panic among the settlers.

We now know that this disease is due to poisoning by a definite compound, tremetol, $C_{16}H_{22}O_3$ (*30*, *31*, *32*), which has been isolated from three plants, white snakeroot (Figure 25) (*Eupatorium urticaefolium*), which causes the disease east of the Mississippi, and jimmy weed (*Aplopappus heterophyllus*) (Figure 26), and a

* E. P. Clarke, personal communication.

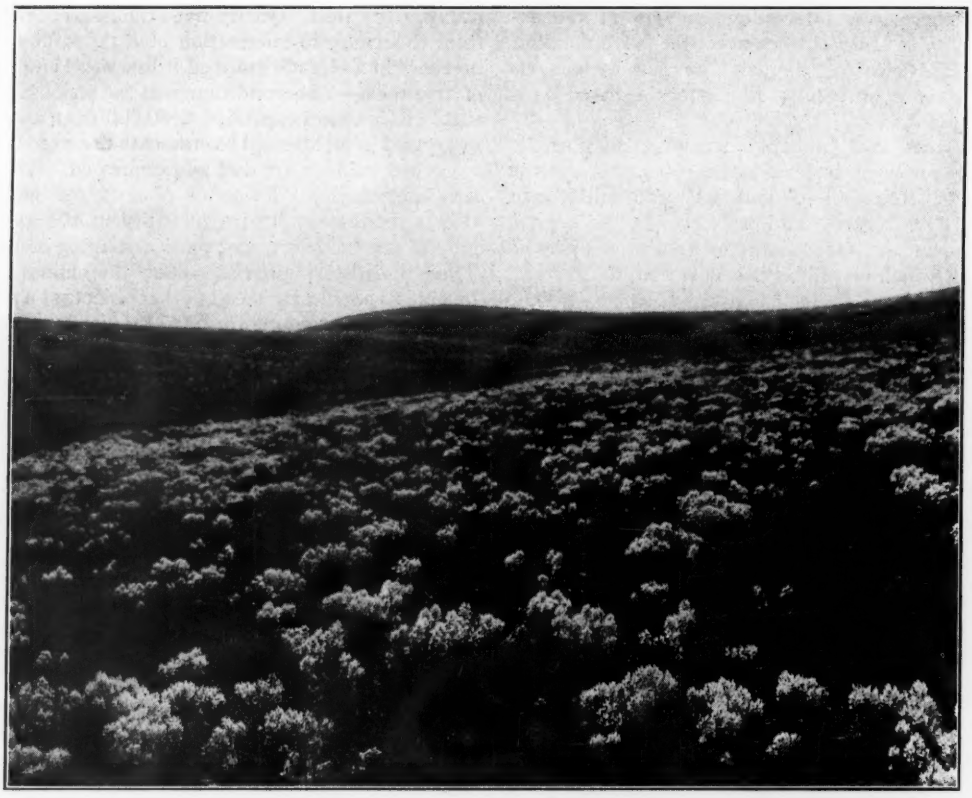


FIGURE 23.—A FIELD OF WHITE LOCO

FIGURE 24.—HORSES SUFFERING FROM LOCOISM

near relative, *A. fruticosus*, which grow in the southwestern states. By feeding upon these plants, livestock contract the disease "trembles," which is characterized by weakness, trembling of the muscles, excretion of acetone, cachexia, and death. Figure 27 shows a sheep in the characteristic attitude of trembles. Milk, butter, and probably cheese made from the milk of cows that have grazed on these plants are capable of transmitting the disease to persons and to animals.

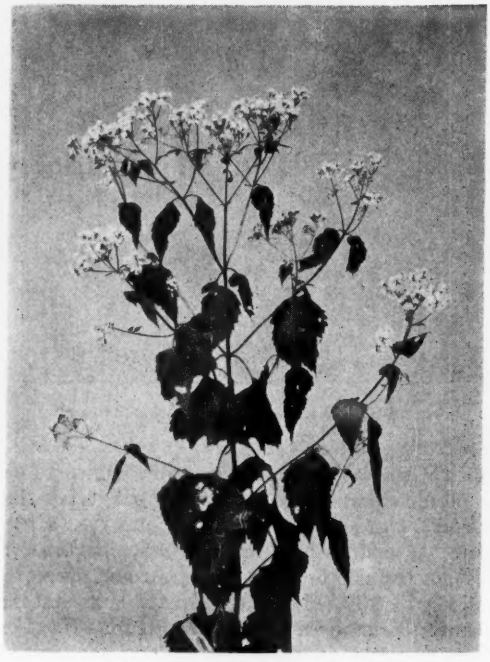


FIGURE 25.—WHITE SNAKEROOT, *Eupatorium urticæfolium*

Suckling calves and lambs are frequently affected in this way. The disease is now of comparatively rare occurrence, since cultivation of the soil destroys the plants that contain the poison.

FIGURE 26.—JIMMY WEED, *Aplopappus heterophyllus*

As members of this group may also be mentioned the active principles of sweet clover (*Melilotus* sp.) brake (*Pteridium aquilinum*), and buttercup (*Ranunculus* sp.).

FIGURE 27.—A SHEEP SUFFERING FROM TREMBLES

SELENIUM

No discussion of poisonous plants would be complete without some reference to the recent developments concerning the ability of certain plants to take up from the soil sufficient quantities of selenium, where present, to render the plants distinctly toxic to animals (*12*, *6*). It appears that some plants not otherwise toxic become so when grown on seleniferous soils, and other plants, like woody aster (*Aster parryi*), may have their toxic properties increased. At present little is known about the chemistry of the poisonous selenium compound in these plants. Other trace elements in the soil may likewise be taken up by plants in much the same way and cause poisoning.

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REGULATING BEAKER STAND

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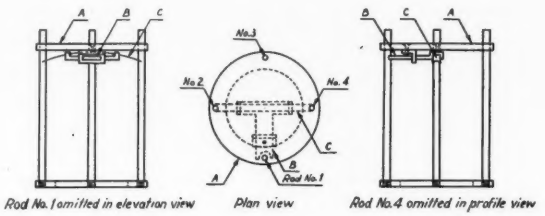
THE device is very useful in quantitative analysis determinations which require filtering through Witt filters into beakers of different sizes, where loss of filtrate, due to dropping from the funnel-end and splashing, jeopardizes the reliability of results. It is made so that it can fit inside a standard Witt filter flask. Any size beaker which ordinarily fits in a Witt filter flask can be used with this device. If a determination requires filtering into a small beaker, the plate *A*, on which the beaker rests, may be raised by pressing upward on a metal strip *B*, which releases the spring *C* from the rods on which it presses. When the metal strip is released, the weight of the beaker plus the tensile strength of the spring prevents the movable plate from sliding. To lower the plate, the same procedure may be followed. The apparatus is made of a resistive metal: brass, for instance, except the spring, which is made of spring steel. The two rods on which the spring presses, and the two guiding rods are threaded at one end and screwed into tapped holes in the bottom plate.



A PROJECT *for* GENERAL CHEMISTRY STUDENTS: COLOR TONING *of* PHOTOGRAPHIC PRINTS

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A GROUP of freshmen, wishing to take part in the Intercollegiate Science Conference,* undertook the color toning of some photographic prints, a project suggested by an article appearing in *Nature Magazine*.[1] Most of the work was done by four students,† one of whom wrote and presented a paper describing the methods used and explaining the chemical reactions involved. The work consisted in preparing solutions, toning and drying the prints, and mounting them on posters, and took about four evenings' time. Since the effects produced were pleasing and the chemical reactions involved were among those usually studied in a general chemistry course, or similar in character, it was thought that others teaching or studying chemistry might be interested in an account of the work.

As is generally known, the process of developing and fixing a print leaves a silver image on the paper. The toning processes used consist of converting the silver of the image into silver sulfide (sepia tones), cupric ferrocyanide (red or reddish-brown tones), ferric ferrocyanide (Prussian blue), or a mixture (green)[2] of iron (blue) and vanadium (yellow) ferrocyanides. The color can be suited to the particular picture at hand, or an interesting series of prints can be obtained by taking several copies of the same picture and toning all but one to the various colors desired.

A half-dozen prints of each of four campus scenes were made, in postcard size, by a commercial photographer. In the case of each photograph, one print was kept in its original form and the others subjected to the various toning processes discussed in this paper. After toning, each set of prints was mounted on a large sheet of cardboard. The four posters thus obtained showed in a striking way the different effects possible. A fifth poster consisted of a sheet of cardboard with labeled vials attached, each vial containing the precipitate corresponding to one of the tones on the prints.

The toning baths were prepared according to formulas given in a pamphlet issued by the Gevaert Company.[3,4] In each case the print was soaked for a short time in water, then immersed in the toning bath, with constant rocking, and finally washed in running water and dried. The work was carried on under artificial light or diffuse daylight.

From the three methods for obtaining sepia prints described in the Gevaert pamphlet, the sulfide redeveloper or "indirect sulfur" process was chosen because it could be used at room temperature. In this method the prints are first "bleached" in a bath containing potassium bromide and potassium ferricyanide. The latter compound is reduced to potassium ferrocyanide, the silver being converted to silver ferrocyanide, then to yellowish silver bromide. After a short washing to remove the potassium ferrocyanide, the print is immersed in a bath of dilute sodium sulfide, which changes the silver bromide to the less soluble silver sulfide.[5,6] The final color and quality of the print depend on the condition of the baths and the length of immersion. The color varies from light brown, when fine particles are formed, to black tones, when the silver sulfide is formed in coarser grains. If the print is removed from the first bath before bleaching is complete, a darker sepia tone results. Moreover, the technic used in the exposure and development of the print is of great importance. The most satisfactory results are obtained when prints are fully exposed and developed before toning; over-exposed and underdeveloped prints yield "washed-out" tones.[7] A sulfide print is quite permanent, more so, if anything, than the original silver image.[8]

* A one-day program of papers and exhibits by students in eleven New England colleges, held annually since 1931.

† Marjorie Hanson, Jeanette Hoffman, Jane Hutchinson, Jane Meyer.

[1] BROWN, SAMUEL, "Photographic notes," *Nature Mag.*, **25**, 50 (Feb., 1935). Mr. Brown was most helpful in giving advice and also in furnishing literature on photography.

[2] NEBLETTE, C. B., "Photography, its principles and practice," D. Van Nostrand Co., New York City, **1927**, ch. XX.

[3] "Formulas for Gevaert films, plates, papers," The Gevaert Company of America, Inc., 423–439 West 55th Street, New York City, **1933**, pp. 23–6.

[4] Slightly different toning formulas are given in the following: FRAPRIE, FRANK R., "How to make prints in colors," American Photographic Publishing Co., 428 Newbury St., Boston, **1916**, pp. 27–32.

[5] MEES, C. E. K., "Fundamentals of photography," 5th ed., Eastman Kodak Co., Rochester, N. Y. (Mar., 1931), pp. 98–9.

[6] FLINT, WILLIAM RUTHVEN, "Chemistry for photographers," 2nd ed., American Photographic Publishing Co., Boston, **1916**, p. 122.

[7] BROWN, SAMUEL, private communications to the author.

[8] SEYEWETZ, A., "Les methodes actuelles de virages en diverses couleurs des papiers photographiques aux sels d'argent," *Chimie et Industrie*, **5**, 3–10 (1921).

The other tones were obtained by the use of baths which contained potassium ferricyanide as oxidizing agent, a metallic salt whose ferrocyanide is insoluble, and an organic acid (or its salt) which, by complex ion formation, retards the deposition of the colored ferrocyanide.[7] In each case the bath was prepared in three parts which were mixed just before use. As in sulfide toning, the preliminary reaction consists in oxidation of the silver to silver ferrocyanide with accompanying formation of potassium ferrocyanide. The potassium ferrocyanide then gives a colored ferrocyanide with the metallic salt.

The blue toner consists of: part "A", a solution of ferric ammonium citrate; part "B", which contains potassium ferricyanide; and part "C", which is diluted acetic acid. The print is rocked in the bath until the image is bright blue, then washed in clear water until the highlights are clean. Rather light prints and short toning give the best results, since the blue toner slightly intensifies the image. Prolonged toning is likely to tint the highlights; this can be remedied by washing in a very weak alkaline bath.[7]

The choice of ferric salt is important, ferric chloride, for example, not serving since it forms silver chloride. It should be completely free of ferrous salt or the bath will contain ferrous ferricyanide, which will tint the whites of the image.[8]

The red toner consists of the following: part "A", potassium citrate solution; part "B", copper sulfate solution; and part "C", potassium ferricyanide solution. Potassium citrate prevents the precipitation of cupric ferricyanide without causing, as would sodium citrate, solution of cupric ferrocyanide.[8] Short immersion gives a warm black, while prolonged immersion continues the reaction, producing a fine red chalk shade. Various intermediate shades of purple, brown, and red may be obtained. Thorough washing follows. "Vigorous" prints are needed for attractive tones.

The green toner is a mixture prepared from: part "A", a solution of oxalic acid, ferric chloride, and ferric oxalate; part "B", potassium ferricyanide solution; part "C", a solution of vanadium chloride and hydrochloric acid. The print is toned until deep blue, then washed until the tone changes to green. Short toning and washing are best; longer toning gives a brighter green, longer washing gives a yellower tone. A very strong print is needed for good results. On account of partial washing away of the image, these were the least satisfactory prints obtained. However, the prints used in the toning were rather weak at the start. An "improved vanadium toning bath" which has not been tested in our laboratory is described by van Beugen.[9] A yellowish stain in the whites may be removed by immersion in ammonium thiocyanate solution.

The stability of iron or vanadium toned prints over a period of years is doubtful. However, care in washing all soluble products out of the prints[6] lessens the tendency toward deterioration. A thin coating of varnish or gum[10] or of a one per cent. benzine solution of paraffin[11] has been suggested as protection against atmospheric action.

It is possible to tone prints with more than one color. This may be accomplished by painting the parts not to be toned with a spirit varnish, such as white shellac. After toning in the first bath the varnish is removed from the untoned part of wood alcohol. The toned portion is next protected by varnish and the toning process continued in the second color.[1] It is well to varnish the back of the print, to prevent penetration of the toning solution from behind.

Numerous other toning processes are described in the literature, involving, for example, the use of uranium, molybdenum, cobalt, lead,[8,10] and selenium[12] compounds as well as the gold and platinum processes commonly used in commercial photography. The references which have been cited in this paper contain a great deal of information which anyone undertaking the toning of prints would find of value. Various precautions generally mentioned in the literature include the following: in preparing the original print, avoid the use of an old fixing bath since this may lead to stains in toning, resulting from the silver compounds present in a used bath; completely remove all hypo by washing, to prevent its action on the silver ferrocyanide formed during the toning process; use matt or semimatt paper in preference to glossy papers, which are more difficult to work with and give less uniform results; in all toning processes, use "vigorous" prints (that is, prints with good contrast). For a good blue-toned picture, the print should be made somewhat lighter than a print which is to be toned any other color. It is also well to experiment on a few old prints to learn proper timing for the color tone desired.

It must be recognized that because of the complexity of photographic reactions in general and the great number of variable factors, the chemical reactions taking place on a photographic print are probably not in all cases exactly the same as the corresponding test-tube reactions. This explains a divergence of opinion about the products formed among some who have investigated ferrocyanide toning processes.[13]

[9] VAN BEUGEN, E., "Improved vanadium toning bath," *Focus*, **20**, 39 (1933) (through *Chem. Abstr.*, **27**, 2642[1] (1933)).

[10] WALL, E. J. AND F. J. MORTIMER, "Dictionary of photography," 11th ed., Iliffe and Sons, Ltd., London, **1927**, p. 639.

[11] PIZZIGHELLI, G., "Leitfaden der praktischen Photographie," 14th ed., by Paul Hanneke, Wilhelm Knapp, Halle-Saale, **1919**, p. 277.

[12] VAN BEUGEN, E., "Tests with selenium toning bath," *Focus*, **20**, 72–4 (1933) (through *Chem. Abstr.*, **27**, 2642[1] (1933)). Also later papers by the same author.

[13] See, for example, (in addition to the references already given) the following: (*a*) NAMIAS, R., "Toning with ferrocyanides," *Atelier Phot.*, **15**, 4 (Dec., 1907) (through *Chem. Abstr.*, **2**, 1390[5] (1908)); (*b*) LUMIERE, A. AND L., AND A. SEYEWETZ, "Composition of silver images toned with metallic salts," *Wiener Mitt.*, **13**, 254 (June) (through *Chem. Abstr.*, **2**, 2655[7] (1908)); (*c*) LEHMANN, E., "Copper toning as a means of mordanting for dye images," *Phot. Ind.*, **1924**, 526–7 (through *Chem. Abstr.*, **19**, 218[1] (1925)).

CORRESPONDENCE

A NOTE ON THE PREPARATION OF *m*-DINITROBENZENE

To the Editor

DEAR SIR:

Meta-dinitrobenzene is a preparation which is included in almost every course of organic preparations which a junior student is expected to go through. All the books which we came across recommend the use of fuming nitric acid for the preparation of meta-dinitrobenzene from nitrobenzene. This is likely to create an impression that without the use of fuming nitric acid (sp. gr. 1.52), the second nitro group cannot be introduced.

Once when we suddenly found that we were short of fuming nitric acid, we used ordinary concentrated nitric acid (sp. gr. 1.42) to see whether it could be substituted if the amount of sulfuric acid was increased. We found that fuming nitric acid was not at all indispensable.

The following table gives the proportions recommended in the literature and those tried by us, with the yields given in each case.

	Nitrobenzene (g.)	*Nitric acid* (g.)	*Sulfuric acid* (g.)	*Yield* (g.)
Gattermann "Die Praxis des Organischen Chemikers"	10	15 (fuming)	25 (conc.)	10–12
Sudburough and James "Practical Organic Chemistry"	10	17.5 (fuming)	20 (conc.)	12
Our experiments	10	15 (sp. gr. 1.41)	25 (sp. gr. 1.82)	4
	10	15 (sp. gr. 1.41)	30 (sp. gr. 1.82)	9
	10	15 (sp. gr. 1.41)	35 (sp. gr. 1.82)	11.5
	10	15 (sp. gr. 1.41)	40 (sp. gr. 1.82)	12
	10	15 (sp. gr. 1.41)	50 (sp. gr. 1.82)	12
Theoretical	10			13.6

It would be interesting to note that fuming nitric acid is eight per cent. dearer than ordinary concentrated nitric acid (sp. gr. 1.42) and that concentrated sulfuric acid is seventy per cent. cheaper than fuming nitric acid.

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SEPARATION OF MAGNETIC PARTICLES UNDER THE MICROSCOPE

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THE separation of magnetic particles from a mixture is an operation frequently attempted under the microscope. Chamot and Mason[1] list several pertinent references dealing with the subject. In all cases the use of a small, permanent magnet, or an electromagnet is advocated. Their use presents the serious difficulty that though the magnetic particles are separated from the mass of material they cannot be readily isolated and recovered, due to the fact that the particles themselves become magnetized and tenaciously adhere to the magnet.

The difficulty is readily eliminated by covering the magnet with glass. The protected, magnetic pole of the magnet can then be inserted directly into a drop of acid and the metallic particles dissolved or the particles can be brushed loose by means of a platinum wire or washed free of attachment with a fine stream of water.

The figure shows a suggested type of apparatus which can be modified to suit the experimental conditions.

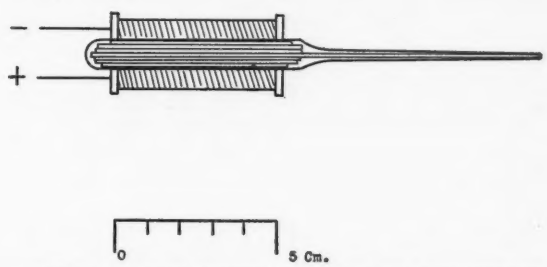

FIGURE 1.—CROSS SECTION DRAWING OF AN APPARATUS FOR THE SEPARATION AND RECOVERY OF MAGNETIC PARTICLES UNDER THE MICROSCOPE

The thick portion of the tube is wound with several layers of Number 30 wire and connected to a dry cell. Two fiber guards are cemented to the tube to hold the layers of wire in place. The thick portion of the tubing covered by the wire contains several iron wires to reinforce the magnetic field of the single iron wire extending to the tip of the thin section of the tube.

[1] CHAMOT, E. M. AND MASON, C. W., "Handbook of chemical microscopy," Vol. 1, John Wiley & Sons, Inc., New York City, 1930, p. 200.

CRYSTAL CHEMISTRY

V. THE PROPERTIES OF BINARY COMPOUNDS

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AS WE study the influence of the structure of a solid upon its properties, it is well to have a clear understanding of the general picture of a crystalline solid. We shall approach the subject from the standpoint of crystals in which the bond is predominantly ionic, since the more familiar inorganic binary compounds fall in this group.

In an ionic crystal, the forces which determine its strength or stability are largely electrostatic; the interionic distances and the crystal radii of the ions are determined by an equilibrium between this Coulomb force, the attractive force of oppositely charged particles, and the repulsive interaction between electrons, resulting from the overlapping of electron clouds as two nuclei approach each other. The relative magnitude of the ionic forces may be predicted in a general way from properties of the ions—their size, valence, and electronic structure. The magnitudes of the ionic forces determine the strength and stability of the crystal. It follows that any properties, physical or chemical, which have any relation to the building up or tearing down of the crystal must be dependent upon the strength and, in turn, upon the size, valence, and structure of the ions of which the crystal is composed. Such properties are: lattice energy; heat of formation; heat of sublimation; heat of combustion; heat of hydration; compressibility; hardness; ionization; melting point, boiling point; solubility; hydrolysis, acidity, basicity.

As the nature of the bond departs from the pure ionic and the bond is more or less homopolar, certain characteristic properties suggest, in a very general way, a loosening of the electrons of the bond holding the ions together. We shall find that this partial change in bond type is related to such properties as ionic diffusion, color, photochemical sensitivity, and photoelectric conductivity. Many of the above properties which measure the strength of crystals are also affected.

In the following pages, an attempt will be made to correlate with the sizes and polarization properties of their ions some of the important properties of ionic or semi-ionic crystals; and to show that it is possible, in general, to predict the properties of any binary compound from these known properties of its building stones. Some of the very fundamental relations between ionic structure and properties will be considered rather superficially, since their detailed treatment is somewhat involved. It must be remembered that the main purpose is to demonstrate the general usefulness of the principles of crystal chemistry, and to this end the relation between ionic structure and the so-called macroscopic properties of compounds (melting point, boiling point, solubility, hardness, hydrolysis, acidity, color, photochemical sensitivity, etc.) which are familiar to the average student of inorganic chemistry will be emphasized.

LATTICE ENERGY

The lattice energy of an ionic crystal is the energy change when a number of positive and negative ions, separated by an infinite distance, are brought together in a crystal lattice, separated by the finite distance, r, the interionic distance in the crystal. The attractive force of two oppositely charged ions with valences Z_1 and Z_2 and at a distance r from each other is $(Z_1Z_2e)/r$, where e is the unit of electrical charge (4.770 E.S.U.). But in a crystal lattice we must consider more than two ions. In the NaCl structure, for example, each sodium ion is coördinated to six chloride ions in the first sphere and twelve sodium ions in the next sphere, eight chloride ions in the third, and so on. These interact upon each other in such a way that the potential

$$\phi = \frac{-e^2}{r}\left(\frac{6}{1} - \frac{12}{\sqrt{2}} + \frac{8}{\sqrt{3}} \cdots\cdots\right),$$

in which the summation is endless. This summation does not depend upon the distance between ions in the crystal, but only upon the geometric arrangement of these ions. It may be represented by a constant, A, known as the Madelung constant (*86*), the value of which depends upon the crystal lattice, as shown in Table 26. The attractive potential, then, of ions in a crystal lattice may be written

$$\phi = -\alpha^2 e^2 \mu A / r$$

where α is the largest common factor of the valences of the ions, and μ is the number of molecules in the unit cell.

But there is also a repulsive force between neighboring ions of opposite charge, the influence of which is to be considered in determining the lattice energy. This repulsive force is similar to that operating between atoms in a noble gas which gives rise to the b term in van der Waals' equation. In a crystal in equilibrium the attractive and repulsive forces must be balanced, and this balance is related to the distance, r, between the ions. The repulsive forces may be assumed to decrease as the distance, r, increases. Taking this force into consideration, the following expression may be derived (see *87*, *88* for a detailed treatment of this derivation) for the lattice energy of a crystal:

$$U = \frac{\alpha^2 e^2 NA}{R_0}\left(1 - \frac{1}{n}\right), \qquad (1)$$

where R_0 is the characteristic equilibrium distance, N

is the Avogadro number and n is a constant determined from the compressibility of the crystal. Values for n have been obtained for the alkali halides by several investigators, as shown in Table 27* (*87, 89, 90, 91*). It is evident that n depends upon the size of the ions.

Recently a new expression for lattice energy has been derived (*92*) in which the nth power repulsive term is replaced by an exponential term. A term also is added to include van der Waals' attraction energy between the ions.

TABLE 26

MADELUNG CONSTANTS (SHERMAN)

Structure	*A*
NaCl	2.201785
CsCl	2.035356
Sphalerite	2.38309
Wurtzite	2.386
Fluorite	7.33058
Rutile	7.70
Anatase	8.04
CdI_2	6.21
Beta quartz	9.5915
Corundum	45.825

TABLE 27

REPULSIVE EXPONENTS FOR ALKALI HALIDES

	n (Slater)	*n (L-J)*	*n (Pauling)*	*H*
LiF	5.9		6.0	He 5
LiCl	8.0		7.0	Ne 7
LiBr	8.7		7.5	Ar, Cu+
NaCl	9.1	9.0	8.0	Kr, Ag+ 10
NaBr	9.5	9.0	8.5	Xe, Au+ 12
NaI		10.0	9.5	

Consider how the lattice energy varies with the structure and arrangement of the ions in a crystal.

Evidently the valence is the most significant term in the equation for lattice energy; U increases with an increase in valence as a result of the increase of α^2. In a rather indirect manner an increase in valence also increases A in some cases as shown in Table 26. Lattice energy also increases as the distance r between the ions decreases; it increases with decreasing cation and anion radii. Small ions can be closer together, and as the distance between them decreases, the attractive force increases. That the effect of the valence upon lattice energy is much greater than that of interionic distance is shown by the following comparative values. Thus, for a maximum difference in interionic distances, we have

	A-X	*U*
LiF	2.008Å.	240.1 kcal.
CsI	3.95	136.1

but for a change in valence, with little change in A-X distance

LiF	2.008	240.1
MgF_2	1.99	695.0
MgO	2.10	940.1

Values for the lattice energies (and other thermal properties) of typical binary compounds are given in Tables 28 and 28A (from Sherman, *loc. cit.*). An inspection of these values shows that:

1. The theoretical lattice energy is slightly higher for compounds with B-cations than for compounds with A-cations of the same size and valence.
2. A difference in the interionic distance does not cause as great a difference in the lattice energies of compounds with B-cations as in the lattice energies of compounds with A-cations. Thus

$$U_{NaCl} - U_{NaI} = 19.6$$
$$U_{AgCl} - U_{AgI} = 11.4$$

3. A comparison of $U_{exp.}$ and $U_{theor.}$ suggests the nature of the bonding forces. Since U is calculated

TABLE 28

DATA FOR THE BORN-HABER CYCLE FOR TYPICAL BINARY COMPOUNDS (SHERMAN)

Crystal	a_0	n	U_0	U	Q	I	S	D	E
LiF	4.02	6.0	238.9	240.1	144.7	123.8	38.3	32.2	98.9
NaF	4.619	7.0	213.8	215.0	136.6	118.0	26.0	32.2	97.8
KF	5.33	8.0	189.2	190.4	134.5	99.6	21.7	32.2	97.6
RbF	5.63	8.5	180.6	181.8	132.8	95.9	19.9	32.2	99.0
CsF	6.008	9.5	171.6	172.8	131.5	89.4	19.1	32.2	99.4
LiCl	5.143	7.0	192.1	193.3	97.5	123.8	38.3	28.9	95.2
NaCl	5.628	8.0	179.2	180.4	98.2	118.0	26.0	28.9	90.7
KCl	6.277	9.0	163.2	164.4	104.9	99.6	21.7	28.9	90.7
RbCl	6.54	9.5	157.7	158.9	104.9	95.9	19.9	28.9	90.7
CsCl	4.112	10.5	147.7	148.9	106.6	89.4	19.1	28.9	95.1
LiBr	5.49	7.5	181.9	183.1	83.7	123.8	38.3	26.9	89.6
NaBr	5.962	8.5	170.5	171.7	86.3	118.0	26.0	26.9	85.6
KBr	6.586	9.5	156.6	157.8	94.2	99.6	21.7	26.9	84.6
RbBr	6.854	10.0	151.3	152.5	96.1	95.9	19.9	26.9	86.3
CsBr	4.28	11.0	142.3	143.5	97.5	89.4	19.1	26.9	89.4
LiI	6.00	8.5	169.5	170.7	65.0	123.8	38.3	25.4	81.8
NaI	6.462	9.5	159.6	160.8	69.5	118.0	26.0	25.4	78.1
KI	7.05	10.5	147.8	149.0	78.9	99.6	21.7	25.4	76.6
RbI	7.32	11.0	143.0	144.2	80.8	95.9	19.9	25.4	77.8
CsI	4.56	12.0	134.9	136.1	83.9	89.4	19.1	25.4	81.7
MgO	4.208	7.0	938.9	940.1	146	520.6	36.5	59.2	−178
CaO	4.802	8.0	840.9	842.1	151.7	412.9	47.5	59.2	−171
SrO	5.15	8.5	789.7	790.9	141	383.8	39.7	59.2	−167
BaO	5.53	9.5	745.8	747.0	133	349.0	49.1	59.2	−157
MgS	5.19	8.0	777.1	778.3	82.2	520.6	36.5	66.6	−72.4
CaS	5.68	9.0	720.6	721.8	114	412.9	47.5	66.6	−80.8
SrS	6.01	9.5	686.2	687.4	113	383.8	39.7	66.6	−84.3
BaS	6.37	10.5	654.7	665.9	111	349.0	49.1	66.6	−80.2
CaSe	5.912	9.5	697.6	698.8	88.4	412.9	47.5	55	−95
SrSe	6.23	10.0	665.9	667.1	90.1	383.8	39.7	55	−99
BaSe	6.59	11.0	635.9	647.1	88.2	349.0	49.1	55	−96

TABLE 28A

Crystal	n	U_0	Q	I	S	E-D	Uexp.	Utheor.	*Dev.*
AgF	8.5	206.7	48.7	173.6	67	66.3	223.0	207.9	15.1
MgF_2	7.0	695.0	264.3	520.6	36	132.6	688.8	696.8	−8.0
CaF_2	8.0	615.9	289.4	412.9	47	132.6	617.2	617.7	−0.5
SrF_2	8.5	585.7	289.3	383.8	39	132.6	580.2	587.5	−7.3
BaF_2	9.5	554.6	281.6	349.0	49	132.6	547.1	556.4	−9.3
MnF_2	8.0	654.5	170.9	532.5	74	132.6	645.0	656.3	−11.3
FeF_2	8.0	655.9	154.2	560.9	94	132.6	676.3	657.7	18.6
CuF_2	8.0	691.8	160.7	578.9	82	132.6	692.9	689.6	−4.7
NiF_2	8.0	695.3	187.8	593.3	85	132.6	733.5	697.1	36.4
CdF_2	8.5	626.9	172.5	594.6	27	132.6	661.9	628.7	33.0
PbF_2	9.5	578.9	159.4	515.5	47	132.6	589.7	580.7	9.0
CuCl	9.0	204.9	32.5	177.3	82	63.6	228.1	206.1	22.0
AgCl	9.5	186.1	30.3	173.6	67	63.6	207.3	187.3	20.0
TlCl	10.5	158.1	48.7	140.2	46	63.6	170.9	159.3	11.6
$SrCl_2$	9.5	491.8	197.7	383.8	40	127.2	494.0	493.6	0.4
CuBr	9.5	196.5	24.6	177.3	82	60.2	223.6	197.7	25.9
AgBr	10.0	180.1	23.9	173.6	67	60.2	204.3	181.3	23.0
TlBr	11.0	153.7	41.0	140.2	46	60.2	166.6	154.9	11.7
CuI	10.5	186.5	15.8	177.3	82	53.8	221.2	187.7	33.5
AgI	11.0	174.7	15.1	173.6	67	53.8	201.9	175.9	26.0
TlI	12.0	147.2	30.1	140.2	46	53.8	162.1	148.4	13.7
CdI_2	11.0	475.2	48.9	594.6	27	107.6	563.1	477.0	86.1
PbI_2	12.0	459.1	41.8	515.5	47	107.6	497.1	460.9	36.2

* The table is reproduced from Sherman, *Chem. Rev.*, **11**, 93 (1932). Pauling's values have been averaged from the suitable values in the last column, thus Na^+ has the Ne configuration and Br^- the Kr; hence n for NaBr is found to be $\frac{7+10}{2} = 8.5$, as given under Pauling.

on the assumption that the crystal is ionic, fair agreement for $U_{exp.} - U_{theor.}$ suggests bonds essentially ionic. Increasing positive values for this sum, however, indicate the influence of electron-pair bonds. When the Born-Mayer equation for lattice energies is used, in which a term for van der Waals' attraction is included, the values for $U_{theor.}$ for the silver halides are higher (*93*) and the $U_{exp.} - U_{theor.}$ is very much less. There is the implication that the influence of the electron pair bond in these crystals is not as great as is implied by Sherman's values.

This relation between A- and B-cations may be attributed in part to the fact that because of the influence of the covalent bond the B-cations have low compressibilities (see Table 31), and therefore higher values for n (see Table 27). For Na^+ (radius = 1.00 Å.), n = 7, while for Ag^+ (radius = 1.00 Å), n = 10. From equation (1) it may be seen that an increase in n causes a slight increase in U, and that since the term $(1 - 1/n)$ becomes nearer unity, an increase in n also reduces the effect of a change in the other terms of the equation upon the value of U.

The influence of crystal structure upon the Madelung constant and thus upon lattice energy is evident from Table 26.

At this point it is interesting to digress for a moment to consider another indirect means of indicating the relative importance of the ionic and the covalent bonds in compounds in which both bond types exist. Pauling has amassed empirical data to show that covalent bond energies are additive. For compounds, then, in which the actual bond energy is greater than that predicted by the addition of the covalent bond energies of the atoms involved, the difference may be taken as a fair measure of the ionic component of the bond. Series of familiar compounds are given in Table 29 (*94*, *95*).

TABLE 29

COVALENT BOND ENERGIES IN VOLT ELECTRONS

	H:H	F:F	Cl:Cl	Br:Br	I:I	K:K
Bond Energy	4.44	2.80	2.468	1.962	1.535	0.51 ± 0.02
		HF	HCl	HBr	HI	
Actual	6.39	4.38	3.74	3.07		
Prepd. from Additivity		3.62	3.45	3.20	2.99	
		2.77	0.93	0.54	0.08	
			KCl	KBr	KI	
Actual			4.5	3.9	3.25	
Prepd. from Additivity			1.53	1.24	1.03	
			3.0	2.7	2.22	

HEATS OF FORMATION

When two elements unite to form a compound, a definite amount of heat is evolved, known as the chemical heat of formation. This is a fair measure of the stability of a compound* because, to decompose it into its uncharged elements the same amount of heat must be added. In building a compound from its elements there are several energy changes, the magnitudes of which may be given in heat units. These changes are represented by the Born-Haber cycle.

$$\begin{array}{ccc} [M] + \tfrac{1}{2}(X_2) & \xrightarrow[-\frac{1}{2}D_{X_2}]{+S_M} & (M) + (X) \\ \uparrow -Q & & \downarrow +I_M - E_X \\ [MX] & \xleftarrow{-U_{MX}} & (M)^+ + (X)^- \end{array}$$

Starting from the upper left-hand corner with the elements, and going clockwise, S_M = heat of sublimation of the metal, D_{X_2} = heat of dissociation of the non-metal, I_M = ionization potential of the metal, E_X = electron affinity of the non-metal, U = lattice energy of the crystal, and Q = heat of formation. In accordance with the law of the conservation of energy, the total energy change must be zero; that is,

$$-Q = S + D + I - E - U.$$

In Table 30 is shown the part played by each of these terms in determining the heats of formation, or stabilities, of typical binary compounds. A positive sign means that energy is absorbed in the process; a negative that energy is evolved.

TABLE 30

THE BORN-HABER CYCLE FOR TYPICAL IONIC COMPOUNDS

	S	*D*	*I*	*E*	*U*	*Q*	*A-X*	R_A	R_X
NaCl	26	29	118	− 91	−180	− 98	2.81Å.	1.00Å.	1.81Å.
KCl	22	29	100	− 91	−164	−105	3.14	1.33	1.81
KI	22	25	100	− 79	−148	− 79	3.53	1.33	2.20
AgCl	67	29	174	− 91	−207	− 30	2.77	1.13	1.81
BaO	49	59	349	−171	−747	−133	2.77	1.31	1.40

Values for *S*, *D*, *I*, *E*, *U*, and *Q* are in kcal.

These compounds have been chosen to show the trend of the terms involved, with the ionic properties: size, valence, and electronic structure. A comparison of NaCl and KCl suggests variations in the terms with the size of the cation, while a comparison of KCl and KI shows the effect of a change in the size of the anion. A comparison of NaCl and BaO indicates the influence of valence and a comparison of NaCl and AgCl shows the effect of the electronic structure of the ion. Of course, to establish a definite trend, a longer list of compounds must be examined. Table 28 shows such a list, from which it may be observed that there are very definite relations between the nature of the ions in a compound and the magnitudes of the thermochemical properties tabulated.

The heat of sublimation (S) and the heat of dissociation (D) are not, of course, properties of the ions. The former is concerned with the metallic state and varies directly with the melting point of a metal, as may be seen from the data in Table 31 (*87*). These terms are relatively small and show little variation.

Evidently ionization potential (I) and electron affinity (E) are very important in their influence upon the stability of a crystal. For ions of equal valences, the more easily a metal atom gives up its valence electrons, and the greater the attraction of a negative

* More precisely, the free energy of formation measures the stability, but the heat of formation is adequate in most cases and is a more convenient quantity to use.

$F = Q - TS$, where F = free energy
Q = heat of formation
TS = an entropy term

atom for electrons, the greater will be the heat of formation and stability of the compound.

TABLE 31
THERMAL DATA FOR METALS

Metal	Melting Point, °K.	Heat of Fusion	Heat of Vapor	Heat of Sublimation at 25°C.	Heat of Sublimation at 0°K.
Aluminum	932	2.35	52	55	55
Antimony	903	4.5	43	49	
Arsenic	1090	5.6	23.2	30.4	
Barium	931	1.40	46	49.1	
Cadmium	595	1.50	25.2	27.2	27.2
Calcium	1083	3.14	42.6	47.5	47.4
Copper	1356	2.70	77.0	81.9	81.6
Gold	1336	3.15	85.0	91	91
Lead	600	1.20	46	47.4	47.6
Magnesium	923	1.70	33.6	36.5	36.3
Mercury	234.4	0.55	14.7	15.2	15.4
Molybdenum	2895	8.38	140	155	155
Nickel	1725	4.25	77	85	
Palladium	1822	3.65	110	118	
Platinum	2046	6.26	116	125	125
Potassium	336	0.57	21	21.6	21.8
Rubidium	311	0.55	19.3	19.9	
Silicon	1688	3.71	79	85	84
Sodium	371	0.63	25.2	26	26
Silver	1234	2.60	63	67	67
Tin	505	1.66	75	78	78
Tungsten	3655	11.2	186	210	210
Zinc	692	1.74	29.1	31.6	31.5

The ionization potential of a metal decreases as the size of the cation increases; K^+ has a lower ionization potential than Na^+. A comparison of the data for NaCl and BaO shows that I increases with the valence of the ion. I is evidently greater for B-cations than for A-cations, as may be seen by comparing NaCl and AgCl.

The electron affinity (E) of the negative element usually cannot be determined directly. It is calculated from the Born cycle when the other terms are known. For the halogens, E decreases as their size increases; that is, other things being equal, the smaller halogen tends to form the most stable crystalline halide. The electron affinities of the divalent $O^=$, $S^=$, and $Se^=$ are opposite in sign to those of the halogens, because heat is absorbed in attaching a second electron to a particle already made negative by the addition of the first electron.

The heat of formation, like the lattice energy, increases as valence increases and as the radius of the anion decreases. With a decrease in the cation radius, however, the heat of formation decreases, while lattice energy increases. There are three conflicting forces in operation here, as may be seen from the data for the alkali halides in Table 28. As the size of the cation increases the ionization potential decreases, which tends to increase stability; with increasing size of the anion, the electron affinity decreases, which tends to reduce stability, and the resulting increase in interionic distance makes for a smaller lattice energy.

Consider again the equation for the Born cycle,

$$Q = -I + U + E - D - S,$$

and substitute for $I = \frac{e^2}{r_M} N$, which says, simply, that the ionization potential is a function of the radius of the metal, r_M. For U, substitute $\frac{e^2 N}{r_A + r_X}$, since, with the valences constant, the lattice energy of a given crystal structure depends almost entirely upon the interionic distance. Then we have

$$Q = \left(-\frac{e^2}{r_M} + \frac{e^2}{r_A + r_X}\right) N + E - D - S.$$

It is evident that if the halide is varied, as in the series NaF, NaCl, NaBr, NaI, in going from F^- to I^-, E is decreased and r_X is increased. This means that Q will be decreased. But if the size of the cation is increased, as in the series LiCl, NaCl, KCl, RbCl, then r_M increases and r_A increases only slightly faster, and the term $\frac{e^2}{r_A + r_X} - \frac{e^2}{r_M}$ will increase. The heat of sublimation will also vary, but to a much smaller degree. Therefore, an increase in the size of the cation causes an increase in the stability (heat of formation) of the compound, but a decrease in the lattice energy, $\frac{e^2}{r_A + r_X}$.

This influence is evident in the data for U and Q in Table 28. It is also true that the hydrogen halides are less stable than the corresponding alkali halides, due, again, to the small cations in the former. This relationship holds for a complex ion such as the trinitride. The acid is explosive; the alkaline earth salts are fairly stable [$Ba(N_3)_2$ decomposes at 120°, $Sr(N_3)_2$ at 110°, $Ca(N_3)_2$ at 110°]. The alkali salts are still more stable, except LiN_3, which is explosive. On the other hand, the trinitrides of the B-cations are explosive.

The same stabilizing influence of the larger central atom may be observed in many other instances where the bonds are not particularly ionic. Consider, for example, the fourth group halides: CI_4, which decomposes slowly at room temperature, is least stable; CF_4 is the most stable of the carbon tetrahalides. The silicon tetrahalides are more stable. $SiCl_4$ is stable up to 1100°; $TiCl_4$, $ZrCl_4$, and $HfCl_4$ decompose very little at 2000°. The iodides are much less stable, so that one may prepare the metals directly from these compounds.* Mutual repulsion of the surrounding atoms increases as their sizes increase and probably accounts for the decreasing stability.

The heats of formation, contrary to the lattice energies, are less for compounds with B-cations than for those with A-cations of the same size and valence. The data of Table 30 suggest that this is due primarily to the large ionization potential of an eighteen-electron shell cation.

To summarize, a crystal may be more easily broken down into ions (*i. e.*, has a lower lattice energy) (1) the larger the anion, (2) the larger the cation, (3) the lower the valence. Other things being equal, a compound of an A-cation will ionize more readily than one of a B-cation. A crystal has a stronger tendency to decompose into atoms (*i. e.*, has a lower heat of formation, is less stable) (1) the larger the anion, (2) the smaller the cation, (3) the lower the valence. A compound of a B-cation is less stable than one of an A-cation.

* The stability of the *molecule* discussed here is not to be confused with the stability of the crystals of these compounds, discussed below.

COMPRESSIBILITY

The resistance of a crystal to compression should be determined primarily by the compactness of its building stones. The data presented in Table 32 tend to confirm this viewpoint. For the alkali halides with the NaCl structure, the compressibility increases as the building stones become farther apart. For the cesium and thallous halides with the CsCl structure, the compressibilities are lower than for halides with the NaCl structure. This is consistent with the transition of the rubidium halides from the NaCl structure to the CsCl structure, caused by high pressure and involving a contraction of ten to fourteen per cent. in volume (*96*, *97*). That is, the ions in CsCl are already in a more compact arrangement than in the NaCl structure and are not condensed further by an external pressure as much as the ions in the NaCl structure. The compressibilities of AgCl and AgBr are lower than those of NaCl and NaBr because, although the interionic distances are comparable, the ions have already been drawn abnormally close together in the silver salts as a result of strong polarization and the influence of a covalent bond. In AgI the structure has changed from one in which the coördination number is six to the ZnS structure with a coördination number of four (a less compact structure), and a higher compression is possible.

TABLE 32

COMPRESSIBILITY OF SOLIDS

	F	Cl	Br	I	O	S
Li	1.53	3.50	4.30	7.20		
Na		4.18	5.09	7.1		
K	4.30	5.65	6.68	8.56		
Rb		7.40	7.97	9.54		
Cs		5.90	7.0	9.3		
Tl		4.9	5.3	6.9		
Ag		2.40	2.74	4.11		
Ca	1.23	4.36	4.84			
Sr	3.32	3.32	4.11			
Ba		2.77	3.66			
Cd		5.95				
Zn					0.89	1.30
Pb						1.91
SnO_2	0.49		FeS_2	0.70		
TiO_2	0.59		FeAsS	0.99		

The compressibilities of the alkaline earth halides do not appear consistent, except that they are lower than the alkali halides, a trend to be expected because of their higher valence. Whereas silver halides cannot be compressed as much as the sodium halides, and SnO_2 (B-cation) has a lower compressibility than TiO_2 (A-cation) $CdCl_2$, with a B-cation, has a higher compressibility than $CaCl_2$ with an A-cation. This is worth noting because $CdCl_2$ crystallizes in a layer lattice, a structure weak in one direction.

From the rather meager data available three observations may be made:

1. Other things being equal, the farther apart the building stones in a crystal, the more they can be compressed.
2. The more close-packed the ions (the higher the coördination number), the less can they be further compressed: as illustrated by a comparison of halides with the CsCl structure (C.N. 8) with those of the NaCl structure (C.N. 6), and by a comparison of AgCl and AgBr (C.N. 6) with AgI (C.N. 4), and by a comparison of the compressibility of the fluorite structure with that of the $CdCl_2$ layer lattice.
3. Other things being equal, the more the ions have drawn each other abnormally close together (through polarization or higher valence), the less they can be compressed further.

In short, compressibility is greatly influenced by the arrangement, the close-packing, of the ions. It is influenced by the size and polarization properties of the ions indirectly as these factors influence the crystal structure.

HARDNESS. MELTING POINTS

While resistance to compression is determined chiefly by the compactness of the building stones of a crystal, hardness, or resistance to deformation, is influenced by the distance between building stones and also by the forces between them which prevent adjacent atomic planes from slipping. The breakdown of a crystal by heat (melting), on the other hand, is directly opposed only by the interionic forces. Other factors may affect the melting point indirectly, in so far as they determine the strength of the forces between ions.

The data of Tables 33, 34, 35, 36 have been arranged to illustrate, respectively, the effect of ionic size, valence, the electronic structures of the ions, and crystal structure, upon the hardness and melting points of ionic and semi-ionic crystals. All values for hardness are those of Goldschmidt (*98*). The melting-point data are from the *International Critical Tables* and the Handbook of Chemistry (*99*).

HARDNESS AND MELTING POINT *vs.* INTERIONIC DISTANCE

It is self evident, from the data in Table 33 that the strength of a crystal, as measured by its hardness, de-

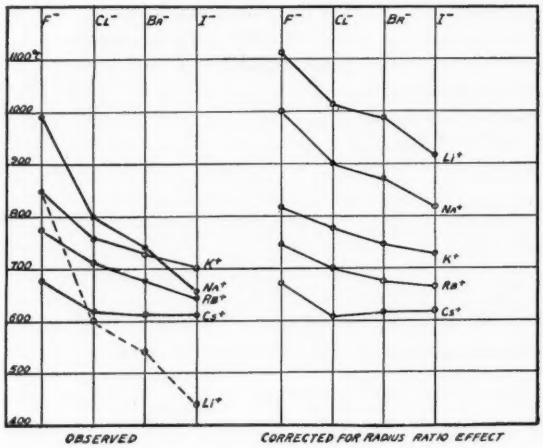

TABLE 33

RELATION OF HARDNESS AND MELTING POINTS TO INTERIONIC DISTANCES

A. Univalent A-cations. NaCl structure. Ionic Bonds. (Hardness only. For melting points, see Figure 12.)

LiF NaF KF

LiCl NaCl KCl RbCl

LiBr NaBr KBr RbBr

NaI KI

Univalent B-cations.

	F	Cl	Br	I	
Cu		2.34	2.46	2.62	Interionic distance in Å.
		2.5	2.4	2.4	Hardness
		422	504	605	Melting point, °C.
		ZnS	ZnS	ZnS	Crystal structure
Ag	2.46	2.77	2.87	2.81	
				1.5	
	435	455	422	552	
	NaCl	NaCl	NaCl	ZnS	

B. Univalent-divalent A-cations. B-cations.

	Mg	Ca	Sr	Ba		Zn	Cd
F	1.99	2.36	2.50	2.68	Interionic dist.		
	4.5	4.0	3.5	3.0	Hardness		
	1396	1330	1190	1280	Melting point	872	520
Cl	712	772	873	962	Melting point	365	568
Br	700	760	643	847	Melting point	394	580
T	dec.	575	402		Melting point	446	385

C. Divalent A-cations. NaCl structure. B-cations.

	Mg	Ca	Sr	Ba		Zn	Cd	Hg
O	2.10	2.40	2.57	2.77	Interionic dist.	1.97		
	6.5	4.5	3.5	3.3	Hardness	5.0		
	2800	2570	2430	1933	Melting point	1800		
S	2.59	2.84	3.00	3.18	Interionic dist.	2.35	2.52	2.53
	4.5	4.0	3.3	3.0	Hardness	4.0	3.2	3.0
	d	d			Melting point	1850	1750	sub. 446
Se	2.74	2.96	3.12	3.31	Interionic dist.	2.45	2.63	2.63
	3.5	3.2	2.9	2.7	Hardness	3–4	3.0	2.8
					Melting point	1100	1350	sub.
Te		3.17	3.32	3.49	Interionic dist.	2.64	2.80	2.79
		2.9	2.8	2.6	Hardness	3.0	2.8	2.6
					Melting point	1238	1041	

D. Trivalent. A-cations. B-cations.

AlP	AlAs	AsSb		GaP	GaAs	GaSb
2.36	2.44	2.64	Interionic dist.	2.35	2.44	2.64
5.5	5.0	4.8	Hardness	5.0	4.2	4.5

E. Tetravalent. Diamond structure.

CC	SiC	SiSi	GeGe	
1.54	1.89	2.35	2.43	Interionic dist.
10	9.5	7.0	6.0	Hardness
3500	2700	1420	958	Melting point.

creases as the distance between the ions increases. This follows for ionic and semi-ionic crystals, for series of different valences and for A-cations or B-cations. In general, the melting points vary in like manner.

The melting points of the alkali halides do not seem to vary consistently with the strength, as measured by hardness. They decrease regularly as the size of the anion increases, but not as the size of the cation increases. The experimental melting points have been plotted in Figure 12. Fajans has accounted for these discrepancies on the assumption that the ions are deformed to some extent (*100*). Pauling has shown (*101*), however, that if corrections are made for the radius ratio effect the variations of the melting points are as in Figure 12. Here the melting points increase as the corrected interionic distances decrease, entirely in accordance with expectations. The same sort of irregularity is encountered with the melting points of the alkaline-earth halides—the change in melting point does not vary consistently with variations in the size of the cations. Possibly a correction for the radius ratio effect is needed in these ionic crystals, the structures of several of which have not yet been determined. Certainly atomic arrangement plays a part in this group. The sharp drop in melting point from MgF_2 to $MgCl_2$, $MgBr_2$, and MgI_2 may be attributed to the layer lattice structure of the last three.

It is of considerable interest to find MgO and CaO very strong, but MgS and CaS easily decomposed. There is no evidence of this weakness in either the heats of formation or the hardness of these compounds.

The high melting points of the tetravalent crystals with the diamond structure, shown in Table 33, are often attributed to their high valence. However, their strengths are probably dependent largely upon the covalent bond and small interatomic distances, since the melting point of germanium (quadrivalent, if ionic) is not appreciably higher than that of univalent CuI, even though the interatomic distance is somewhat larger in the latter. To find that the strength, as measured by melting point, is quite independent of valence is consistent with the existence of the covalent bond in these crystals. But consider the melting points of the divalent compounds of the B-cations which crystallize like ZnS, shown in Table 34. For constant interionic distances, the melting points are more than double those of the corresponding univalent salts. Apparently strength, as implied by melting point, increases, as does the hardness of these same compounds, with an increase in valence. This is difficult to reconcile with a covalent bond and is further evidence of the existence of a bond

TABLE 34

VARIATION OF HARDNESS AND MELTING POINTS WITH VALENCE

A. A-cations. Ionic structures, NaCl, CaF_2, or SnO_2.

Valence	*1-1*	*2-1*	*2-2*	*2-3*	*2-4*	*3-3*	*4-4*	*3-3*	*2-2*
Compound	LiF	MgF_2	MgO	Al_2O_3	TiO_2				
A-X dist.	2.02	1.99	2.10	1.90	1.96				
Hardness	3.3	4.5	6.5	9.0	6.5				
M. P.	870	1396	2800	2050	1640 d.				
	NaF	CaF_2	CaO		ThO_2	ScN	TiC		
	2.31	2.36	2.40		2.42	2.23	2.23		
	3.2	4.0	4.5		6.5	7–8	8–9		
	992	1330	2570		2800		3180		
	NaCl	BaF_2	BaO			AlSb			
	2.81	2.68	2.77			2.64			
	2.5	3.0	3.3			4.8			
	804	1280	1933						

B. B-cations.

CuCl		ZnS		GaP	SiSi			
2.34		2.35		2.35	2.35			
2.5		4.0		5.0	7.0			
422		1850			1420			
CuBr	$CoCl_2$	ZnSe		GaAs	GeGe	AsAl		
2.46	ca.2.50	2.45		2.44	2.43	2.44		
2.4		3–4		4.2	6.0	5.0		
504	sub.	1100			958			
CuI	$CdCl_2$	ZnTe		GaSb				SeCd
2.62	2.66	2.64		2.64				2.62
2.4		3.0		4.5				3.0
605	568	1238						1350
AgI		CdTe		InSb	SnSn			
2.81		2.80		2.79	2.80			
1.5		2.8		3.8				
552		1041						

at least partly ionic. Of course, the melting points of the alkaline earth oxides, in which the bond is strictly ionic, are more than three times those of the alkali halides.

HARDNESS AND MELTING POINTS *vs.* VALENCE (TABLE 34)

Among ionic compounds with A-cations and crystallizing in the NaCl, CaF_2, or TiO_2 structures, there is a rather consistent increase in strength, measured by hardness and melting points, with increasing valence. Dioxides with the rutile structure seem to have consistently low melting points; Al_2O_3 and MgS are also somewhat out of line.

For B-cations, hardness increases regularly with valence. Melting point increases with valence up to the tetravalent metals, if we except $CoCl_2$ and $CdCl_2$, weak layer lattices.

TABLE 35

VARIATION OF HARDNESS AND MELTING POINT WITH ELECTRONIC STRUCTURE

		A-cation			B-cation		
		NaCl structure			ZnS structure		NaCl structure
Univalent		NaF			CuCl		
	A-X	2.31			2.34		
	Hard.	3.2			2.5		
	M.P.	992			422		
		LiCl			CuI		AgF
		2.57			2.62		2.46
		3.0			2.4		
		614			605		435
		NaCl			AgI		AgCl AgBr
		2.81			2.81		2.77 2.87
		2.5			1.5		
		804			552d		455 422
Uni-divalent		CaF_2 structures			CaF_2 structures		$CdCl_2$ structure
		TiO_2			TiO_2		
		CaF_2			CdF_2		
		2.36			2.34		
		4.0			4.0		
		1330			520		
		MgF_2			ZnF_2	MnF_2	
		1.99			2.04	2.16	
		4.5			4.0		
		1396			872	856	
		SrF_2			PbF_2		$CdCl_2$
		2.58			2.58		2.66
		3.5			3.2		
		1280			855		568
		$MgCl_2$ ($CdCl_2$ struct.)					$MnCl_2$
		2.63					2.63
		712					650
Divalent		NaCl structure			ZnS structure		NaCl structure
		CaO					CdO
		2.40					2.34
		4.5					
		2570					1000d.
		SrO	MgS		CdS	HgS	
		2.57	2.59		2.52	2.53	
		3.5	4.5–5		3.2	3.0	
		2430	d.		1750	446 sub.	
		BaO			CdTe	HgTe	PbO
		2.77			2.80	2.79	2.66
		3.3			2.8	2.6	
		1923			1041	....	888
		SrS	CaSe				PbS
		3.00	2.96				2.97
		3.3	3.2				2.8
		d.	d.				1120
		BaS					PbTe
		3.18					3.22
		3.0					2.3
		d.					917
		A-cation					B-cation
Di-tetravalent		SiO_2				GeO_2	
		1.72				1.77	
		7.0				5.0	
	ca.	1700				1100	
Di-trivalent		Al_2O_3				Fe_2O_3	
		1.90				2.10	
		9.0					
		2050				1560	
Trivalent		AlP	AlAs		AlSb	GaP	GaAs GaSb
		2.34	2.44		2.64	2.35	2.44 2.65
		5.5	5.0		4.8	5.0	4.2 4.5
Tetravalent		TiC(NaCl)			SiSi(ZnS)		GeGe(ZnS)
		2.23			2.35		2.43
		8–9			7.0		6.0
		3180			1688		958

HARDNESS AND MELTING POINT *vs.* ELECTRONIC STRUCTURE (TABLE 35)

In comparing the relative hardness and melting points of A- and B-cations, the other variables, valence, crystal structure, and interionic distance, have been held constant. Without exception the compounds of B-cations are weaker, both in respect to hardness and melting points, than are the A-cation compounds. It will be recalled that these compounds also have lower heats of formation and their instability is attributed principally to the difficulty with which the cation ionizes. In short, we are dealing with a semi-ionic, apparently a loosened and weakened, bond.

HARDNESS AND MELTING POINT *vs.* CRYSTAL STRUCTURE (TABLE 36)

Data on this comparison are meager and not very conclusive. The brevity of the list in Table 36 is forced by the necessity of comparing only those compounds in which the other variables, valence, interionic distance, and electronic structure, may be held constant.

TABLE 36

VARIATION OF HARDNESS AND MELTING POINT WITH CRYSTAL STRUCTURE

			NaCl	*vs.*	*ZnS*	
		AgCl	AgBr		AgI	
		2.77	2.87		2.81	
					1.5	
		455	422		552	
			CdO		ZnS	
			2.34		2.35	
					4.0	
			1000		1850	
			MgO		BeS	
			2.10		2.10	
			6.5		7.5	
			CaO		BeTe	
			2.40		2.43	
			4.5		3.8	
		ScN	TiC		AlP	SiSi
		2.23	2.23		2.34	2.35
		7–8	8–9		5.5	7.0
			CaF_2-TiO_2	*vs.*	*$CdCl_2$-CdI_2*	
			BaF_2		$CdCl_2$	
			2.68		2.66	
			3.0			
			1280		568	
			PbF_2		$MgCl_2$	$MnCl_2$
			2.58		2.63	2.63
			855		712	650
			CaF_2	*vs.*	FeS_2	
			2.36		2.28	
			1330		1171	
			NiAs	*vs.*	*ZnS*	
NiS	FeS	CrS	CoS		ZnS	
2.28	2.28	2.28	2.30		2.35	
797	1193	1550	1100		1850	
			NiAs		ZnSe	
			2.44		2.45	
			968		1100	
			NiSb		CdSe	
			2.64		2.63	
			1158		1350	

Several general observations may be made from this table:

1. The transition, NaCl to ZnS structure, apparently has little effect, either on hardness or melting point.
2. The transition $CaF_2(SNO_2)$ to a layer lattice ($CdCl_2$, CdI_2) is accompanied by a marked decrease in strength, as measured by melting point. That the layer lattices are characteristically weak

is shown also in Table 37. The melting points and heats of formation decrease much faster in the transition from fluoride to iodide via the layer lattice than they do for a series of the calcium halides which supposedly will have the fluorite or rutile structure (see Table 37).

3. The NiAs structure appears to be weaker than the ZnS structure; and the FeS_2 structure is weaker than CaF_2 structure. It would be interesting to have more data for these groups.

One would like to know the cause of the wide variation in melting points of CrS, FeS, CoS, NiS, all with the same interionic distance and the same valences; all transition elements and all with the NiAs structure. The melting points do increase consistently as the number of electrons in the *M* shell decreases.

TABLE 37

THE STRENGTH OF LAYER LATTICES

A. Melting points and heats of formation of some halides.

		Ionic Lattice (CaF_2 or TiO_2)				Layer Lattice ($CdCl_2$ or CdI_2)			
		Fluoride		Chloride		Bromide		Iodide	
Ra.		M. P.	Q.	M.P.	Q.	M.P.	Q.	M.P.	Q.
.78	Mg	1396	263.8	712	153.2	700	124.0		
.78	Ni		119.0	sub.	74.5				
.82	Co		179.7	sub.	76.5	d.	72.9		42.5
.83	Fe		177.1		82.0	d.	78.7	177	47.5
.83	Zn	872	144.0	365	99.5				
.91	Mn	856	206.0	650	112.0	d.	107.0	d. 80	76.2
1.03	Cd	520	123.5	568	93.2	580	76.3	385	48.3
1.32	Pb	855	159.4					402	41.8

B. Heats of formation of the magnesium and calcium halides.

	Fluoride	*Chloride*	*Bromide*	*Iodide*
Mg	263.8	153.2	124.0	
Ca	286.3	190.3	169.0	128.6
Sr	289.0	197.8	171	142.5
Ba	287.7	205.3	180.4	144.8

MELTING POINTS OF THE DIOXIDES

The dioxides of quadrivalent elements form an interesting group. In Table 38 the melting points and hardnesses are compared with the interionic distances, electronic structure of the cations, crystal structures, and heats of formation.

TABLE 38

MELTING POINTS AND HARDNESS OF THE DIOXIDES

Formula	A-X	*Electronic Structure of Cation*	*Crystal Structure*	C.N.	M.P.	Hard.	*Q*
SiO_2	1.73	2-8	SiO_2	4	1670	7.0	201.4
GeO_2	1.80	2-8-18	SiO_2	4	1100	5.0	
MnO_2	1.84	2-8-13	SnO_2	6	d.	6–7	126.0
VO_2	1.93	2-8-9	SnO_2	6	1967		209.1
TiO_2	1.96	2-8-8	SnO_2	6	1640 d.	6–6.5	218.4
IrO_2	1.98	2-8-18-32-13	SnO_2				
OsO_2	1.99	2-8-18-32-12					
WO_2	2.00	2-8-18-32-10	SnO_2	6	ox. in air		126.2
SnO_2	2.06	2-8-18-18	SnO_2	6	1127	6–7	138.1
PbO_2	2.16	2-8-18-32-18	SnO_2	6	290d.	5–5.5	62.4
TeO_2	2.21	2-8-18-18-2	SnO_2	6		3.5–3.8	78.3
ZrO_2	2.21	2-8-18-8	CaF_2	8	2700		178.7
CeO_2	2.34	2-8-18-7	CaF_2	8	1950		234.9
UO_2	2.37	2-8-18-32-18-10	CaF_2	8	2176		256.6
ThO_2	2.41	2-8-18-32-18-8	CaF_2	8	2800		330.9

Hardness seems to decrease fairly regularly as the interionic distance increases. Not so, however, for the melting points, which are consistent with the heats of formation; they bear no relation to the interionic distances. In fact, those with the highest melting points are the ones with the largest cations. These irregularities are somewhat reminiscent of those found for the alkali and alkaline-earth halides and may be due to a radius ratio effect. Without question, the melting points, on the whole, increase as the coördination number of the crystal structure increases, those with the fluorite structure being the most stable. The melting points of SiO_2 and GeO_2 are lower, relatively, than would be expected from the small size of the cation, and the low coördination number may have some bearing upon this. There also appears to be some correlation between stability and electronic structure. Those cations with a completed eight- or eighteen- electron shell are, in general, the most stable. PbO_2 may seem contradictory, until one realizes that the Pb^{++} ion is more stable than Pb^{+4}. Among the crystals with the fluorite structure, the relatively low melting points of CeO_2 and UO_2 are consistent with their incompleted outer electron shells.

THE INFLUENCE OF CRYSTAL ENVIRONMENT UPON STABILITY

In a series of compounds like NaF, MgF_2, AlF_3, SiF_4, PF_5, and SF_6, a sudden increase in volatility or decrease in melting point is a direct result of the arrangement of the ions and the distribution of the bonds in the crystal. The argument, briefly, is this: NaF and MgF_2 are typical ionic crystals, throughout which ionic bonds between oppositely charged particles extend in all three crystallographic directions. AlF_3 forms an ionic lattice, but in general the AX_3 compounds are apt to form weakened layer lattices. In SiF_4 there is the possibility of the four fluorines completely surrounding each silicon and screening it so that only a weak residual force extends from the central, electropositive silicon beyond the four electronegative fluorines to attract neighboring molecules. The SiF_4 group may exist as a molecule in the crystal lattice and the forces holding these molecular building stones together will be very weak, making for a weak crystal. To put the matter somewhat more briefly, the sudden change in stability comes at the point where the coördination number of the electropositive element becomes equal to the stoichiometric ratio of X to A in the compound formula (*102*, *103*). Thus, for NaF, MgF_2, and AlF_3 the coordination numbers characterizing the crystal structure are six or eight, while the X:A ratios are 1, 2, and 3 respectively. In SiF_4 the coördination number is 4 as is the X:A ratio.

The sharp change in volatility or electrical conductivity is not necessarily due to a transition from the ionic to the covalent bond, as has been assumed by many investigators (*104*, *105*) although undoubtedly in most cases, the covalent bond assumes increasing importance. Indeed, we know that the strength of the covalent bond is of the same order of magnitude as that of the ionic bond. Biltz and Klemm, who compiled the data in Table 39 for the melting points of the chlorides and the conductivities of their melts, pointed out

that the transition is one from ionic to *molecular* crystals and that the decreased stability is a result of a change from ionic to *molecular* forces.

As a matter of fact, there is no reason to postulate that the bonds in SiF_4 are entirely different from those in AlF_3. It has been suggested, by a wave mechanical treatment, that the bond in SiF_4 is probably partly ionic and partly covalent (*102*). A measurement, by electron diffraction, of the S-F distance in SF_6 suggests that even in this compound (and in SeF_6 and TeF_6) the bond is more ionic than covalent (*106*). Of course, the small fluoride ion has a strong electron affinity and thus a strong tendency to form the ionic bond.

The full effect of the weak molecular force is manifested when the size and number of the negative atoms or ions with respect to the electropositive element to which they are attached are such that the central atom may be completely surrounded and its attractive force effectively screened. Innumerable data are available to demonstrate in a convincing manner the effect of the increasing size and number of the surrounding atoms or ions upon the stability of binary compounds. Some of these are listed in Table 39. The table is practically self-explanatory, and the sudden break in strength in going from left to right along a horizontal row is readily understood. That this break occurs farther to the right for the lower rows is to be expected, for the size of the central atom is increasing from top to bottom. The boiling points of SiF_4, TiF_4, and VF_5 are used for comparison since the melting points of the last two are not available.

TABLE 39

STABILITY OF TYPICAL IONIC AND MOLECULAR CRYSTALS

A. Ionic forces.....Molecular forces.

Melting Points (Figures in parenthesis are boiling points).

LiF	BeF_2	BF_3	CF_4		
870	800	−127	−80		
NaF	MgF_2	AlF_3	SiF_4	PF_5	SF_6
992	1396	1040	−77	−83	−55
			(−65)		
KF	CaF_2	ScF_3	TiF_4	VF_5	SeF_6
880	1330		(284)	(111)	

B. Melting Points and Equivalent conductivities.

LiCl	$BeCl_2$	BCl_3	CCl_4	
613	440	−107	−22	Melting points.
166	0.086	0	0	Equivalent conductivities.
NaCl	$MgCl_2$	$AlCl_3$	$SiCl_4$	PCl_5
800	718	191	−69	148 (pressure)
133.5	28.8	1.5×10^{-6}	0	0
KCl	$CaCl_2$	$ScCl_3$	$TiCl_4$	
768	780	940	−22	
103.5	51.9	15	0	
RbCl	$SrCl_2$	YCl_3	$ZrCl_4$	$CbCl_5$
714	870	<686	>300	194
78.2	55.7			2×10^{-7}
CsCl	$BaCl_2$	$LaCl_3$	$HfCl_4$	$TaCl_5$ WCl_6
645	960	860		211 275
66.7	64.6	29		3×10^{-7}* 2×10^{-6}*
			$ThCl_4$	UCl_5
			810	567
* Specific conductivities			16	0.34^4

C. Boiling Points. (Sidgwick)

AlF_3	$AlCl_3$	$AlBr_3$	AlI_3	
800	183	260	382	Boiling points.
328	166	126	71	Heats of formation.
SiF_4	$SiCl_4$	$SiBr_4$	SiI_4	
−90	57	153	290	Boiling points.
SnF_4	$SnCl_4$	$SnBr_4$	SnI_4	
705	114	202	340	Boiling points.
CCl_4	$SiCl_4$			

In Table 39 the equivalent conductivities of the fused chlorides are given as well as their melting points. The equivalent conductivities were measured just above the melting points, except $BeCl_2$, determined at 35°C. There are sudden breaks in conductivity at $BeCl_2$, at $AlCl_3$ — $SiCl_4$, $ScCl_3$ — $TiCl_4$, etc. This loss of conductivity is frequently pointed out as evidence of a change from an ionic to a covalent compound (*104, 105*). There is no need to assume this. When a crystal melts, it breaks at its weakest link. For $SiCl_4$ and similar crystals the weakest link is a molecular or van der Waals' attraction between $SiCl_4$ molecules. The breakdown of a molecular crystal gives no indication of the nature or strength of the intramolecular forces. A molecular crystal may be very unstable, yet the molecules of which it is built may be very stable and difficult to decompose.* When the molecular $TiCl_4$ crystal breaks down, $TiCl_4$ molecules exist in the melt and the latter is, of course, non-conducting, not necessarily because the intramolecular forces are covalent, but because the mobile units in the melt are neutral molecules.

Table 39C carries on the matter from a slightly different angle. In 39A and 39B, the sudden change in properties comes with a decreasing radius of the electropositive element and the increase in the number of electronegative elements available for screening the central atom or ion. In 39C, the size of the electropositive central element increases, the number and size of surrounding electronegative elements remain constant, and the same abrupt change in properties occurs. Thus AlF_3 is an ionic crystal with a relatively high boiling point, while a sharp drop is encountered in $AlCl_3$, a typical layer-lattice structure. The boiling point increases from $AlCl_3$ to AlI_3, from SiF_4 to SiI_4, and from $SnCl_4$ to SnI_4 are in accordance with the increasing molecular weights in these series. (The boiling points of the aluminum halides are higher than those of the tin halides, probably because the former are polymerized as Al_2X_6.) Thus, if the central atom is so small that it is completely surrounded and screened by the electronegative element, then the boiling point increases in the series F-Cl-Br-I; but if the central atom is not surrounded by fluoride, then the boiling point decreases in the series F-Cl-Br-I until the halide becomes large enough to screen the central atom, and from that point on the boiling point again increases in the normal manner.

The same relation of stability to environment may be observed in a series of the oxyhalides. WOF_4 boils at 190°C., while $WOCl_4$ boils at 227.5°C. One may say that in the fluoride the central atom is completely surrounded and the higher boiling point of the chloride results from its higher molecular weight. But if the central atom is not completely screened in the fluoride, one must expect the chloride to be more volatile; thus VOF_3 boils at 480°C., while $VOCl_3$ boils at 127°C.

* See Table 39C. The boiling points of the aluminum halides are an approximate measure of the relative strengths of the crystals; the heats of formation are a fair measure of the stability of the molecules.

Many other examples of the influence of the relative numbers and relative sizes of atoms or ions upon the stability of their compounds might be given. To mention a few at random:

1. SF_6 is well known, but not SCl_6. SCl_4 is the highest known chloride of sulfur, and S_2Br_2 is the highest bromide known.
2. Similarly, we have MoF_6, but not $MoCl_6$, $MoCl_5$ being the highest molybdenum chloride known.
3. An increase in volatility may be observed in a series of oxides as the relative sizes of the cations increase; but for the oxides the charge on the central atom must be six in order to have three surrounding anions, and the probability of having four screening anions is slight. This accounts, in part, for the relatively small number of gaseous oxides known. Some interesting data are shown in Table 40.

TABLE 40

STABILITY OF TYPICAL OXIDES, AS INDICATED BY MELTING POINT

Na_2O	MgO	Al_2O_3	SiO_2	P_2O_5	SO_3	Cl_2O_7	
subl.	2800	2050	1600	sub. 250	16.8	explosive	
Cs_2O	BaO	La_2O_3	HfO_2	Ta_2O_5	WO_3		OsO_4
subl, 1000	1923	2000	2812	d. 1470	2130		130

In the second row, the cations are larger and the break in stability, suggesting the formation of a molecular lattice, comes farther to the right. In both series the break comes further to the right than with the halides, since the number of halide atoms per central atom may be twice the number of oxygens.

Let us summarize, at this point, the influence of crystal structure, of ionic properties (size, valence, and electronic structure), of bond type, and of the relative number of electronegative elements bonded to each electropositive atom upon the strength and stability of crystals as indicated by compressibility, hardness, melting point, and boiling point.

The resistance of a crystal to compression depends chiefly upon the interionic distances and the crystal structure, the arrangement of the building stones. If the distances are large and the atoms or ions loosely packed (*i. e.*, for structures with low coördination numbers), considerable compression may be expected.

Hardness is a measure of resistance to deformation. This is determined chiefly by the distance between atoms or ions and by the forces holding them together.

Melting point is a measure of the resistance of the crystal to disruption by heat. It is determined primarily by the strength of the bonds within the crystal. This strength, of course, is influenced by interionic distance (in ionic crystals), valence, electronic structure of the ions, the crystal structure, and by the relative number of positive and negative elements coördinated to each positive atom in the crystal. The last factor determines, in most cases, whether or not a weak molecular crystal will be formed.

The data in Tables 33–39 summarize the evidence supporting these generalizations.

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INTERNATIONAL EXHIBITION OF APPLIED AND SCIENTIFIC PHOTOGRAPHY TO BE HELD IN ROCHESTER, MARCH, 1937

An International Exhibition of Applied and Scientific Photography will be held in Rochester in March, 1937, under the sponsorship of the Rochester Scientific and Technical Section of the Photographic Society of America. The objective of the exhibition will be to show examples of the application of photography to the various branches of science and technology. The following sections have been organized: color photography, astronomy and metrology, aerial photography, photomicrography, medical photography, X-ray in industry, documentary photography, high speed photography, stereo-photography, photography in physics and chemistry, photographic sensitivity, natural history, and miscellaneous.

Photographs or apparatus showing the applications of photography to typical problems in any branch of science and technology will be welcomed. All correspondence in regard to the Exhibition, or requests for entry blanks, should be addressed to the Secretary, C. B. Neblette, F.R.P.S., Department of Photographic Technology, Rochester Athenaeum and Mechanics Institute, Rochester, New York.

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KEEPING UP WITH CHEMISTRY

Barium as a chemical raw material. J. J. Riley. *Chem. Industries*, **39**, 13–8 (July, 1936).—Before the War (1914–18) this country had mined crude barytes ore and also ground and bleached some of it and had a well-developed lithopone industry, but barium chemicals were practically all imported. Our supplies were cut off—certain of the chemicals were declared "necessities," and "priorities" were allowed for material to erect factories. This produced the inevitable "war babies," most of which died in infancy. Some of the companies struggled along and survived the post-war period, developed a technic of their own so that we now have an established American industry on both the Atlantic and Pacific coasts, and in between. The American products are as good as the best imported and prices are at a satisfactory basis to both the user and the manufacturer.

This independent American supply is quite a technical achievement of which the country might well be proud, if anything were generally known about it, but barium chemicals are a key-industry necessary to certain manufacturers and quite unknown as such to the general public. Instead of being simply an inert or filler, as in the very early days, the bariums, through improved and cheaper methods and because of better chemical knowledge, have established a position because of their chemical value, and have a bright future. A. T. B.

Staple fiber rayon. H. B. Vallrath. *Chem. Industries*, **39**, 21–3 (July, 1936).—Rayon manufacture by the viscose process (which accounts for about 80–5 per cent. of the world's production) had its inception in the United States only twenty-five years ago. The oldest and largest of our domestic companies began operations in the year 1910 and enjoyed a monopoly for some ten or eleven years until the basic patents they controlled expired. This industry had its beginning in Europe and practically all domestic companies started business either under licenses from older European companies or as American branches of German, Dutch, Belgian, and Italian interests.

The general procedure laid down in those early days was for many years almost exactly copied, the process of making viscose rayon being considered so delicate and troublesome that no one dared do anything radically different. Thus this young industry early became tradition-bound. To cite only two illustrations of remarks which the present author has heard during his fifteen years of contacts in the industry: one European chemist in charge of an American plant, when offered a new and highly improved machine for making viscose solution, said "Viscose is capricious. When I gets her right, I leaves her alone. Your machine may do all you claim, but I am not having trouble today and I am satisfied." Another man, for some years manager of his plant, when asked why he used a corn sugar of a certain specification as one of the ingredients in his coagulating bath in which the viscose is spun into thread, replied, "Because our grandfathers did."

A tremendous amount of rayon research has been going on steadily, and the more progressive, well financed companies have made remarkable strides in improving the uniformity and quality of their yarn. But during the past eight or ten years very little fundamental change has taken place in the chemical side of the process, whereas its mechanical side has seen ingenious improvements making for more economical production and better control of quality. A. T. B.

Oils and fats in the leather industry. Anon. *Chem. Industries*, **39**, 35 (July, 1936).—The chief function of oil in leather manufacture is the lubrication of the collagen bundles which form the larger portion of the hide. These bundles must be lubricated so that they will orient themselves to the stress imposed on the leather and will not glue together to give a hard, brittle product. In the case of some animal oils, there is a combination between the oil and the hide fiber, and in the production of chamois leather, oil is the only tanning agent used.

Tests indicate that the active materials in oil tannage are the unsaturated fatty acids. Most of the active fatty acids in this process have at least two double bonds, and during the tanning they are oxidized to diperoxide structures, reacting with the hide substance to form a compound of collagen and fatty acid. In the course of the reaction some aldehyde, which may be detected by the odor, is liberated, and probably exerts a secondary tanning effect on the hide. A. T. B.

Slime. Its control in paper making by chlorine and ammonia. R. Trautschold. *Chem. Industries*, **39**, 27–9 (July, 1936).—Industrial slimes are caused by microörganisms of a large and prolific bacteria family—by germs which enter tanning, papermaking and other processes with their organic raw materials and via the water supply. These slime organisms abound in Nature. The run-offs in the water sheds bring them into nearly all surface water reservoirs and into most shallow wells, whence they pass into the factory systems. Recent progress in slime control in the paper industry is therefore widely interesting.

The tiny parasites attack the cellulose, causing that material to decompose, and form gelatinous capsules around the organic cells of the bacilli. These deposits grow rapidly when conditions are favorable for propagation. The products of the metabolism are acid (carbonic and lactic), and build up during the life cycle of the organisms, with a resulting lowering of the hydrogen-ion concentration of the solution in which the bacilli breed. This gradual, progressive change in the water's pH value eventually arrests the growth of the bacteria, but then a secondary mold, also highly objectionable, usually develops, living upon the accumulation of gelatinous slime.

This, in brief, is the cycle of slime bacillus activities directly responsible for both losses and expenses in paper making; for impaired quality of product, for waste in contaminated pulp and loss of good pulp and for considerable increase in paper production expenses. Attacks by the slime pests differ widely, depending upon the types of bacteria, but in any event they prove decidedly costly.

Since the offending bacilli cannot be kept out of the paper fabricating processes by physical precautions, they must be destroyed and propagation controlled by chemical means. Special treatments may be required, various kinds and degrees of chemical dosages being needed and the application of the chemicals localized at strategic points to secure the best results; but much has been learned from the purification of potable water supplies.

Effective chemical control of slime is being successfully accomplished in progressive paper mills, chiefly by the use of chlorine, either alone or, as is now held to be the approved method, in conjunction with anhydrous ammonia in chloramine treatments.

Chlorine is an efficient bactericide, but it is also a strong oxidizing agent, combining chemically with various ingredients in the stock suspension. Thus comparatively heavy dosages of chlorine, when that chemical is used alone, are required to effect satisfactory sterilization of the paper stock, since most of the chlorine is consumed and neutralized by substances in the pulp.

Results in many mills, large and small, producing bond and ledger, boxboard, building, and wrapping papers indicate beyond question that the proper application of chloramines provides a positive control over paper slime. With the trend in mill practice definitely toward the increased use of recirculated white water, chloramination, as distinguished from chlorination, marks an important step in the application of industrial chemistry which gives great promise of bringing about substantial savings in one of the nation's major basic industries. A better product at a lower price should result, for a waste burden of millions per year can be much reduced. A. T. B.

The chemical action of the ultra sound waves. H. Schultes and H. Gohr. *Angew. Chem.*, **49**, 420–3 (July 4, 1936).—H_2O_2

in a concentration of 1% is produced by the action of ultra sound waves on water saturated with oxygen. If the water is saturated with air, then HNO_2 is produced in addition to the H_2O_2. In that case, the yellow color of the titanium reaction for H_2O_2 is unstable. In the presence of sufficient O_2 the HNO_2 is oxidized to HNO_3. L. S.

Protection of food and forage. W. R. HAMBY. *Chem. Warfare Bull.*, **22**, 130–3 (July, 1936).—Consumption of food and forage infected with chemical agents caused many casualties during the World War. One instance was noted where over half the horses of a field artillery regiment were sick after grazing in a mustardized area. Any future war between first class powers will undoubtedly see highly developed and specialized chemical attacks. The protection of food and forage then becomes a matter of great importance. The advent of the airplane capable of spraying chemical agents even in rear areas makes the problem more complex.

Foods exposed to contamination by arsenic compounds must be destroyed; chlorine and phosgene may be removed from food by ventilation, although an unpleasant taste remains. Fatty and oily substances are highly susceptible to vapor absorption. Reclamation of infected food is extremely risky. The best rule to follow is: when food and forage have been exposed to chemicals take no chances; destroy them! Generally speaking, the same precautions are necessary to guard against an infected source of water supply. W. O. B.

APPARATUS, DEMONSTRATIONS, AND LABORATORY PRACTICE

A simple apparatus for surface tension measurements. W. E. HASKELL. *Chemist-Analyst*, **25**, 70–1 (July, 1936).—The simple apparatus described here, constructed out of an analytical balance and Autostrop safety-razor blade, is much more rapid than the capillary-rise, drop-weight or drop-number methods, and much less tedious. One pan of the balance is removed, and is replaced by a wire with a hook at each end. Another wire is shaped into an inverted V, with a hook on each end to hook into the notches of the blade. This is then suspended from the balance by means of the first wire. The balance is then brought into equilibrium by attaching a weight of rolled lead to the first wire. The rider is then placed on the side from which the blade is suspended so that the pointer is displaced 1 division mark. The liquid to be tested is then raised until contact is made with the blade. Weights are then added until the blade is just pulled loose.

The surface tension $= \frac{(W - W_1)g}{2L}$, when W = weights added, W_1 = weight of rider, g is 981 dynes, and L the length of the blade. The blade should be carefully cleaned before use. Values within 0.5 dyne of accepted values are possible. D. C. L.

Stainless steel invades laboratory. ANON. *Chem. & Met. Eng.*, **43**, 491 (Sept., 1936).—In its exclusive use as the structural material for all furnishings and equipment in the new analytical laboratory of the Ford Motor Company's River Rouge plant, the alloy has entered one of the few remaining industrial equipment fields which had yet to feel its influence.

Each complete table top is made of $^1/_{16}$ inch stainless steel sheet, prefabricated in one piece. Tables are equipped with built-in sink; downdraft hood; utility shelf; 110-volt and 220-volt electrical outlets; tubing connection outlets for gas, air, water, and vacuum; and tap outlets for hot, cold, distilled, and ice water—all of stainless steel. A sheet form of the metal is also used for continuous wall covering from the red tile floor up to the windows. J. W. H.

A projection spectroscope. R. G. LAFONTAINE. *Rept. New Eng. Assoc. Chem. Teachers*, **38**, 5–6 (Sept., 1936).—The accessories are mounted on a six-foot optical bench. An arc is obtained with 110-volt A.C. and carbons enclosed in a housing. The light passes through a slit, lens, combination liquid and crown glass prism, and a second lens, and then is thrown on a ground glass screen. A fairly long and brilliant continuous spectrum is obtained. Bright line spectra are obtained by drilling the core of one carbon and filling with the desired salt. Reversal of sodium D line is shown by drilling a carbon filling with sodium chloride and mounting a sodium flame before the prism. The mechanism permits many interesting spectral demonstrations on a distant screen by using a projecting lens at the end of the train. W. O. B.

SCIENTIFIC REVIEWS AND BIBLIOGRAPHIC TABULATIONS OF SCIENTIFIC DATA

Modern thoughts on chemical linkage. H. FROMHERZ. *Angew. Chem.*, **49**, 429–37 (July 11, 1936).—A survey dealing with the historical development of the conceptions about atoms and molecules, the quantum mechanics of atoms and molecules and chemical linkage from the standpoint of quantum mechanics, including ion and atom linkages. L. S.

The artificial preparation of the radioelements. I. JOLIOT CURIE AND F. JOLIOT. *Angew. Chem.*, **49**, 367–9 (June 13, 1936).—A Nobel lecture reviewing these authors' own experimental work dealing with the preparation of new radioactive elements by transformation. L. S.

The nature and action of ferments. H. ALBERS. *Angew. Chem.*, **49**, 448–55 (July 11, 1936).—A review. One hundred references. L. S.

How the synthesis of caoutchouc originated. See this title under Keeping Up with Chemistry.

HISTORICAL AND BIOGRAPHICAL

Science in a changing world: recollections and reflections. R. GREGORY. *Nature*, **137**, Suppl., 981–8 (June 13, 1936).—In this lecture at the Royal Institution, Sir Richard Gregory, who has been on the editorial staff of *Nature* for more than forty years, discussed some of the important discoveries which were first announced in that journal. Lord Rayleigh's famous letter in which he requested an explanation for the higher density of atmospheric nitrogen as compared with that of nitrogen he had prepared from its compounds was published in the issue for September 29, 1892. After Lord Rayleigh and Sir William Ramsay had explained this anomaly and brought to light the inert gas argon, Ramsay examined the gas in the mineral cleveite and at first believed it to be a new gas, krypton, for which he had been searching. Sir William Crookes showed spectroscopically, however, that cleveite contains a gas identical with the helium which Sir Norman Lockyer and P. J. C. Janssen had independently observed twenty-seven years earlier in the sun's spectrum. On March 28, 1895, Ramsay's statement was published in *Nature* under the title "Terrestrial Helium (?)."

W. C. Röntgen's discovery of the X-rays was communicated to the Würzburg Physical Medical Society near the end of 1895, and full translation of the paper appeared in *Nature* for January 23, 1896. The first suggestion for the application of cathode rays to oscillograph tubes for the transmission and reception of images was made by Mr. Campbell Swinton in *Nature* of June 18, 1908. This is the basis of modern systems of television. Langley's paper on "Experimental researches on mechanical flight" was communicated to the Paris Academy of Sciences on July 13, 1891, and a translation of it appeared in *Nature* ten days later. M. E. W.

The place of science in general history. F. S. M. *Nature*, **138**, 575–6 (Oct. 3, 1936).—Until recently, most writers of

general history have had little or nothing to say about the achievements of science. F. S. M. believes that the overpowering emphasis on the governmental side of history must be corrected and that the change must take place gradually. The new spirit of history was well expressed by Lord Acton of Cambridge. In the "Cambridge Modern History," separate chapters on science, written by specialists, have been included. This, however, "does not meet the need of synthesis in treatment" nor does it show "how the scientific spirit has made itself felt in the realms of government, religion, or social life." G. N. Clark in his "History of the Seventeenth Century" has been very successful in writing the scientific portions himself. Preserved Smith's "History of Modern Culture" goes to the extreme of "not preserving any political outline" and "rather loses the sequence and position of events." F. S. M. believes that it is most important to enlist the general historians in this cause, for they "have the historical spirit and the technique. . . . An alliance between the two forces and an enlargement of the old historical discipline would be an educational revolution of the most far-reaching type." M. E. W.

Daniel Gabriel Fahrenheit (1686–1736). ANON. *Nature*, **138**, 428–9 (Sept. 12, 1936).—The German physicist and instrument-maker, D. G. Fahrenheit, was born in Danzig on May 24, 1686 and died in Holland on September 16, 1736. His excellent thermometers were known the world over. Galileo, Boyle, Huygens, Hooke, and Halley all contributed to thermometry, but ". . . Ferdinand II, Grand Duke of Tuscany (1610–70) . . . was the first to produce a thermometer unaffected by atmospheric pressure."

Fahrenheit devised his well-known scale about 1714 and was the first to bring the mercurial thermometer into general use. Professor Ernst Cohen and W. A. T. Cohen-de Meester have recently published a biographical memoir in the *Transactions of the Royal Academy of Sciences of Amsterdam* which shows that Fahrenheit lectured and wrote on hydrostatics, optics, and chemistry and was highly esteemed by the scholars of his day. A letter which he wrote to Boerhaave in 1729, which was recently discovered in Leningrad, tells of his visit in 1708 to the Danish astronomer Römer, who aroused his interest in thermometry. The bicentenary memoir contains portraits of Boerhaave, Römer, s'Gravesande, Musschenbroek, and Nieuwentyt, but Professor Cohen was unable to find any likeness of Fahrenheit himself. M. E. W.

Dr. Edward Weston. A. R. *Nature*, **138**, 496 (Sept. 19, 1936).—The great pioneer of electrical industry, Dr. Edward Weston, died August 20, 1936. He was born in 1850 on the boundary between England and Wales. At the age of fifteen years he went to the United States, where he studied and improved direct-current dynamos. The Weston cadmium cell as modified through the researches of Sir Frank Smith is a most trustworthy means of measuring voltages. Dr. Weston's moving-coil ammeters, voltmeters, and wattmeters are used throughout the world. He was the first to employ Bakelite on a commercial scale. M. E. W.

TEACHING OBJECTIVES, METHODS AND SUGGESTIONS

Some trends in chemical education. R. A. BAKER. *Rept. New Eng. Assoc. Chem. Teachers*, **38**, 6–15 (Sept., 1936).—The author tries to adjust present trends into the perspective of the past as a guide to the future and finds humor in the situation. A conflict exists between teachers who know a little chemistry and technical chemists who know little of educational psychology. Professional interest in chemical education is encouraging. The author notes a decided swing to microchemistry and predicts that the next revolutionary laboratory manual of general chemistry will be one using micro methods. He also looks for more thermochemical and electrochemical experiments and less analytical chemistry. The photographic film is a great aid, and the sound film holds great possibilities. Clubs and Boy Scouts' activities represent spontaneous interest worthy of careful guidance. Educational psychiatrists have produced many objective chemistry tests, but a most significant trend is in the objectives themselves. The author lists the following in order as desirable outcomes of the introductory cultural chemistry course: (1) development of a sense of matter, (2) vocabulary, (3) technical knowledge, (4) vision of the fields of chemistry. The author advocates laboratory examinations and individual laboratory work rather than lecture demonstrations for developing perseverance, originality, independence, initiative, confidence, and accuracy. Many educators are tending to advocate the elimination of individual laboratory work but others feel that a real understanding of nature can best come through personal experiences in the science laboratory. W. O. B.

GENERAL

Educational topics and events. ANON. *Nature*, **138**, 299 (Aug. 15, 1936).—The Wisconsin Alumni Research Foundation started in 1925 with no invested capital, but only the patent application of Professor Harry Steenbock. The corporation has exploited this patent for the use of ultra-violet rays in enriching the vitamin D content of foods and medicinal products and has profited from other patents similarly acquired from members of the University. In ten years the Steenbock patent alone "has enriched the University by nearly $700,000 and provided an endowment worth more than $125,000 a year for the future needs of research." M. E. W.

Organon. ANON. *Nature*, **138**, 237 (Aug. 8, 1936).—"The first number of a new international review, *Organon*, has been published in Warsaw by the Mianowski Institute." Although all the authors are Polish, it is printed in French and English. In the first contribution, entitled "The science of Science," Drs. M. and S. Ossowski state that the new "science of Science comprises investigations concerning very widely separated subjects and brings them into internal harmony." Other articles are entitled: "The man of action and the student," "Documents on the psychology of invention in the domain of science," "Science and scholarship in Poland to the close of the sixteenth century," and "Organization of Polish science." There are also articles on the two leading Polish scientists, Copernicus and Mme. Curie. M. E. W.

What industry means to America. ANON. *Chem. & Met. Eng.*, **43**, 468–9 (Sept., 1936).—Data are taken from *Factory Management and Maintenance* for August, 1936 as they apply to the chemical industry.

The chemical industries gainfully employ 402,585 with a total payroll of $553,340,129. The value of the products is $3,702,672,063.00. There are 8224 establishments.

As to the use of research it is pointed out that 93.6% in 267 companies have produced new products commercialized during the past two years; 83.7% in 273 companies rely upon research for technical developments; and 62.8% in 247 companies have made technical developments useful to other industries. J. W. H.

Scientists and war. C. N. ACHARYA. *Nature*, **138**, 469 (Sept. 12, 1936).—On August 22 prominent scientists of India met under the joint auspices of the Institute of Chemistry of Great Britain and Ireland and the Society of Biological Chemists to discuss the moral responsibility of scientists in modern warfare. The meeting passed a resolution which pledges its support "to every united effort which can be made to abolish methods of warfare which are repugnant to the common instinct of humanity, [but] recognizes that the more important objective is the abolition of war itself." It recommends "the study of means for controlling the evil effects of mass suggestion by the more powerful agency of widely disseminated right ideas through the adoption of an international system of education." M. E. W.

Science at the International Peace Congress. C. DOVER. *Nature*, **138**, 516–7 (Sept. 19, 1936).—"Scientific concern for the preservation of world peace found abundant expression at the International Peace Congress held at Brussels on September 3 to 6. . . . The joint commission on science and war is to include chemists, physicists, engineers, aeroplane technicians, doctors, bacteriologists, geologists, and military experts. . . . The committee concerned with the fundamental causes of war . . . will . . . neglect no opportunity to expose pseudo-scientific and pseudo-historical theories used for war propaganda. . . ." M. E. W.

RECENT BOOKS

ELECTRON DIFFRACTION. *R. Beeching*, A.R.C.S., B.Sc., Imperial College of Science and Technology, Aberdeen, Scotland. Chemical Publishing Co. of N. Y., Inc., New York City, 1936. viii + 107 pp. 39 figs. 10 × 17 cm. $1.25.

This little book gives a brief account of the major points pertaining to the subject of electron diffraction. In the first chapter there is a derivation of Schrödinger's equation, a discussion of waves and particles, and a treatment of the diffraction of a plane wave by a crystal. Chapter II deals with the discovery of and the early work on electron diffraction and some of the general principles underlying the problem. Diffraction by thin films and by gases is discussed in Chapter III. The simple theory for the intensity of the diffracted radiation in terms of the atomic structure factor is derived, and methods of measuring the factor are taken up. Experimental results for the scattering by monatomic and polyatomic gases and the theory for determining atomic spacings in the latter cases have been treated in a satisfactory manner. In the next chapter, diffraction by reflection from crystal planes is taken up and it is shown how the relaxation of the Bragg conditions leads to a variety of diffraction patterns. A few pages are given over to the theory and experimental determination of the inner potential. The last two chapters deal with apparatus and technic and with practical applications to such problems as lubrication, oxide layers, polished surfaces, etc., for which electron diffraction methods are ideally suited.

The field of electron diffraction has grown to the point where it may be difficult to give an entirely satisfactory account of it in a book of this size. It is felt, however, that the book might have been materially improved by shortening some parts and lengthening others. Some of the derivations might have been omitted or simplified and the space used for a more complete discussion of experimental results. For example, the discussion of the crystal as a grating and the derivation of Bragg's law could be shortened. The discussion of the early work of Davisson and Germer would have been improved by the inclusion of one or two diagrams. The chapter on applications could have been made more detailed. These points are not, however, of major importance. A point which seems to detract considerably from the understandability of the volume is the fact that *there is not a single reproduction of an electron diffraction picture.* In many cases those which are described verbally are by no means easy to picture in one's imagination. On the title page the book purports to have a halftone frontispiece but there was no sign of such a page in the reviewer's copy. A single page with a number of small reproductions would have materially improved the book. Aside from the above-mentioned criticisms the book presents the facts in a clear way. It is an interesting introductory outline of the subject and should prove helpful to anyone who plans to utilize the methods of electron diffraction for the study of surface phenomena.

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PROCEEDINGS OF THE SECOND DEARBORN CONFERENCE OF AGRICULTURE, INDUSTRY, AND SCIENCE. Farm Chemurgic Council and The Chemical Foundation, Inc., Dearborn, Michigan. xii + 409 pp. 16.5 × 25.5 cm. $0.50 postpaid.

This record of the Proceedings of the Second Dearborn Conference contains the following chapters: Contents—Introductory; Council Luncheon; Opening General Session; Symposium on New Things; Power Alcohol; Starch and Sugars; Plastics; Cellulose; Farm Chemurgic Banquet; Soy Bean; Insecticides and Fertilizers; Closing General Session; Business Session; Appendix.

THERMIONIC EMISSION. *T. J. Jones*, M. Sc., Research Physicist for Lissen Ltd., London, and for Pye Radio Ltd., Cambridge. First edition. The Chemical Publishing Co. of New York, Inc., New York City, 1936, viii + 108 pp. 17 figs. 10 × 17 cm. $1.25.

Comparing this small volume with the more comprehensive work published by A. L. Reimann two years ago, it appears that the author has accomplished an excellent task in condensing the 324 pages of Reimann's book. While, as a consequence, the various topics are discussed more briefly, the monograph is very readable and should provide the general reader, whether chemist or physicist, with a survey over the field of thermionic emission.

The contents of the different chapters are indicated by the following headings: I. Introduction (historical); II. Theory of the Thermal Emission of Electrons (including emission equations, Schottky effect, and the "Shot" and "Flicker" effects); III. Experimental Technique and Electron Emission Data for Clean Metals; IV. Atomic Film Emitters (Thorium and Caesium); V. Oxide-Coated Emitters; and VI. The Thermal Emission of Positive Ions. A bibliography of references to seven general publications and to 149 papers completes the volume. In a future edition mention should be made of the volume on "Electron Emission and Adsorption Phenomena" by J. H. de Boer, published in 1935.

The book contains a few misprints and small errors. Some investigators would question the validity of the Schottky equations to very low field strengths. Furthermore, the value of the book would have been increased by addition of a few tables giving actual emission data (amps./cm.^{2} as function of T) for some of the materials used in practice, instead of leaving it to the reader to calculate such data from the values of the emission constants.

On the other hand, the chapter on oxide-coated cathodes is an excellent summary of the mass of conflicting data found in the literature.

The reviewer has no hesitation in recommending the volume to those who desire a survey of the subject from a general point of view, and not from that of the specialist in the particular field.

SAUL DUSHMAN

GENERAL ELECTRIC COMPANY
SCHENECTADY, NEW YORK

MODERN ALCHEMY. *Dorothy M. Fisk.* D. Appleton-Century Co., New York City, 1936. xiv + 171 pp. 18 figs. 13.5 × 20 cm. $1.75.

In this intriguing little book, the author has rather skilfully presented in popular style the present-day status of nuclear atomic phenomena. To create the proper background for recent developments, the narrative opens some 2500 years B.C. when the alchemists along the Nile began their unsuccessful search for the Philosopher's Stone for converting baser metals into gold and historically carries the reader rapidly up to and through those early days when Roger Bacon, Boyle, Newton, Dalton, and a host of others were laying the foundations of the atomic theory of today. Then, with the discovery of the electron, X-rays, and natural radioactivity, the narrative moves more slowly, tracing the further developments of atomic structure, the early transmutations produced by Rutherford and his co-workers, the discovery of "heavy" hydrogen, the neutron and the positron, and closes with the more recent work on transmutations that led to the discovery of artifical radioactivity by Irene Joliot Curie and F. Joliot in 1934 and the syntheses of new isotopic elements.

The book is quite accurate and up to date. Miss Fisk, always keeping the non-specialist reader in mind, has used many homely

illustrations and analogies to explain and clarify the principles and methods employed in this rapidly developing field. However, with ideas and theories constantly undergoing modification, the author possibly may be accused of being slightly dogmatic in occasional definitions and statements. A thoroughly interesting and illuminating book for both teacher and student.

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BAYLEY'S CHEMISTS' POCKET BOOK. Edited by *Robert Ensoll*. E. & F. N. Spon, Ltd., London. Chemical Publishing Co. of N. Y., Inc., New York City (American agents). Ninth edition, 1936. xv + 460 pp. 10 × 16.5 cm. $3.50.

This handbook is actually compact enough to be carried in the pocket by anyone who can do things like that and still keep peace with his tailor. It is divided into seven sections as follows.

I. Mathematical (pp. 2–24)
II. Weights and Measures (pp. 26–52)
III. Physical
- (*a*) Reduction of the Volume of Gases to Normal Temperature and Volume (pp. 54–72)
- (*b*) The Barometer (pp. 73–9)
- (*c*) Hygrometry (pp. 81–2)
- (*d*) Tables for the Conversion of Thermometric Degrees (pp. 84–5)
- (*e*) Miscellaneous tabulations of physical constants and conversion factors, formulas, etc. (pp. 86–221)

IV. General Analysis
- (*a*) Preparation of Reagents (pp. 224–31)
- (*b*) Qualitative Analysis (pp. 232–49)
- (*c*) Indirect Analysis (pp. 250–7)
- (*d*) Methods and data pertaining to analysis of specific commodities (pp. 257–92)

V. Gravimetric Analysis (pp. 294–337)
VI. Volumetric Analysis (pp. 338–411)
VII. Miscellaneous (pp. 412–51)

The work is well indexed and impresses one as a useful and inexpensive aid for the practical chemist.

OTTO REINMUTH

GENERAL CHEMISTRY. *Harry N. Holmes*, Professor of Chemistry in Oberlin College. Third edition. The Macmillan Company, New York City, 1936. viii + 700 pp. 200 figs. 14.5 × 21.5 cm. $3.50.

Textbook authors have responded in various ways to the current demand for "modernization" of the general chemistry course. To some, modernization has meant inclusion of the newer discoveries in experimental chemistry without any change in viewpoint; to others it has meant an increasing emphasis on physical chemistry with an ever-decreasing attention to descriptive chemistry. In this revision of his *General Chemistry*, Professor Holmes has chosen a middle course. He describes the book as "modern, but not radical." New developments in industry (*e. g.*, advances in petroleum refining, recovery of bromine from the sea, and the Downs process for sodium) and new discoveries in pure science (heavy hydrogen, artificial transmutation, etc.) are adequately discussed, as well as the recent theories of solution and of acids and bases. The classical Arrhenius theory is retained, but the discussion of it is augmented by a summary of the Debye-Hückel theory. An entire chapter is allotted to Brønsted's theory of acids and bases, so that the teacher may include or omit it, as he sees fit. Except in this chapter, the older views of acids and bases are used throughout. Thus, a teacher wishing to use Brønsted's views will probably have to teach the older theory first.

The electron theory of atomic structure is very briefly discussed in Chapter III, and is used frequently throughout the book, but it cannot be said that Professor Holmes teaches chemistry from the atomic structure "point of view." In fact, the orbital arrangement of the electrons is first discussed near the middle of the book. The approach to the concepts of chemistry must, therefore, remain largely historical. For example, the defects of Mendeléeff's periodic system are pointed out and are later explained away by the introduction of atomic numbers. The atomic-structure approach would derive the periodic system from the electron shells, and thus seek to avoid the defects.

Professor Holmes' books are characterized by his lucid and readable literary style, which is probably the greatest element in their success. This book is a splendid example of his work, and should do a great deal to make the study of chemistry attractive to those who use it. The numerous pictures and diagrams help materially in this respect.

Each chapter in the book is supplemented by a list of exercises and a group of references for further reading. The references are well chosen, and should be of great value both to students and teachers. Some of the early chapters contain chapter outlines to assist the student in learning how to study. The appendices and other study helps are very similar to those used in the earlier edition.

The author is not always careful to define new terms as he introduces them. For example, the word "hydrolysis" is used on pages 177 and 190, but is explained on page 226. The word "ion" appears on page 139, although the student is taught nothing of the concept of ionization until he reaches page 202.

A person making a critical study of *any* textbook will find some features which he would wish changed, and this book is no exception. However, the reviewer feels that Professor Holmes has fulfilled his purpose very well and has produced a book which deserves wide popularity.

JOHN C. BAILAR, JR.

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EXPERIMENTAL ENZYME CHEMISTRY. *Henry Tauber*, Ph.D., New York Homeopathic Medical College. Mimeoprint edition. Burgess Publishing Co., Minneapolis, 1936. vi + 118 pp. 16 figs. 20 × 28 cm. $3.50.

The book is primarily a review of recent progress in the study of enzymes, with brief introductory citations of earlier work for perspective. Each section is accompanied by a well-selected bibliography, citing, in most cases, the original description of each enzyme, methods of measurement, reaction characteristics, and methods of preparation. Of the 118 pages, 37 are used for references and 15 for introductory theory. Something of the consequent brevity in discussions may be indicated by the number of pages allowed for each section, as follows: esterases 4, proteases and peptidases 22, amidases 7, carbohydrases 12, catalase 2, oxidizing enzymes 13, carbonic anhydrase 2, zymase 3, and luciferase 2. One page of errata has been attached. The author has briefly indicated the nature of published procedures for experimentation, leaving all details to be sought in the references. The book is essentially well prepared and will serve as a valuable reference to supplement the older and more detailed books.

C. G. KING

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DOCTORAL DISSERTATIONS ACCEPTED BY AMERICAN UNIVERSITIES, 1935–1936. *Donald B. Gilchrist*, Editor. The H. W. Wilson Company, 950–72 University Ave., New York City, 1936. 102 pp. Paper, $2.00.

This is the third of these annual lists, compiled for the National Research Council and the American Council of Learned Societies, by the Association of Research Libraries; Donald B. Gilchrist, editor.

No list of similar scope has previously appeared for American dissertations, although complete lists for French and German

university dissertations have been published annually for many years.

Of the many dissertations accepted each year only about one-third ever appear in print. Also universities now make it an almost universal practice to file full manuscript theses in duplicate, and to make copies available through inter-library loan. For these reasons this publication is a necessary one.

In form, the list is very similar to, and continues, the annual list in the field of science, issued since 1920 by the National Research Council. Its scope has been broadened to cover all fields of study; and that there may be no break in the statistical record, the dissertations in the field of science have been classified in the same subject groups used in the N.R.C. series, those for other fields being selected on much the same basis.

For greater convenience, the list has been arranged in seven main divisions: Philosophy, Religion, Physical sciences, Earth sciences, Biological sciences, Social sciences, Literature, and Art. While the arrangement is an arbitrary one, it follows in a general way the organization of American universities into divisions and departments, and the finding of material is further facilitated by a general subject cross-index and an author index. When theses appear in print, mention of this fact is made also.

Each annual number contains, as supplementary material, records of previous theses lists, annual lists of doctoral dissertations in progress, statistical tables showing doctorates in science according to subject, and distribution of doctorates by university by subject. There is also a table showing the present practice in all universities whose theses are listed, as to the publication and loaning of their own dissertations. The publishers suggest that libraries wishing to order these lists annually as they appear file continuation orders with them for the series.

CATALYTIC REACTIONS AT HIGH PRESSURES AND TEMPERATURES. *Vladimer N. Ipatieff*, formerly Professor at Artillery Academy, St. Petersburg, now Professor at Northwestern University, and Director of Chemical Research, Universal Oil Products Co. The Macmillan Co., New York City, 1936. xii + 786 pp. 55 figs. 14 × 22 cm. $7.50.

This book is unique in its purpose and in its execution. The author says of it in his foreword, "This book is my chemical autobiography. For that reason no attempt was made to collect the literature or to include the work of others except in special cases where it was desirable to emphasize and develop certain features, or where it was considered to have a direct bearing upon my own researches." There are, however, about nine hundred references to the work of some four hundred fifty authors, exclusive of the author's co-workers.

Two great names stand out in catalysis: Sabatier and Ipatieff. Sabatier is far better known; his researches were published in French, and he wrote a remarkable book on catalysis, published in 1920 and translated into English and German. The two investigators started at nearly the same time and covered much the same ground but were guided by different theories and employed different methods. Sabatier's experiments were made at atmospheric pressure commonly with gases or vapors; Ipatieff usually worked with liquids under high pressures, measured in tens or hundreds of atmospheres, and at higher temperatures. Ipatieff's investigations were published almost exclusively in Russian, and, though they were known to the world through the abstract journals and were mentioned by other authors (forty-three times in Sabatier's book), few outside of his own country have realized the extent and the importance of his pioneer work. He was the first to hydrogenate in the liquid phase and to study promoters.

As should be in an autobiography the chapters are arranged chronologically. The first nine chapters with the periods that they cover are: I. Dehydrogenation 1901–1902; II. Dehydration of alcohols 1901–1904; III. Decomposition of acids 1903–1904; IV. Isomerization 1904–1906; V. Hydrogenation 1905–1906; VI. Promoters 1911; VII. Hydrogenation of amines and metallo-organics; VIII. Destructive hydrogenation; and IX. Condensation. The earlier chapters are valuable for reference, as they bring out the historical development of ideas and methods, but make tedious reading, as each experiment is described in detail with weight of material taken, amount of catalyst, temperature and time of heating, initial and final pressures, amount of product and boiling ranges of the fractions obtained from it, analyses of the gases and other data. A large part of the 167-page chapter on hydrogenation is devoted to experiments bearing on the relative efficiencies of reduced nickel and of nickel oxide.

Chapters X and XI on theories of catalysis and on polymerization are more modern and of more timely interest. The importance of water, both in hydrogenation and in oxidation, is strongly emphasized. Chapter XII is on catalytic alkylation and XIII on destructive alkylation. The book closes with an appendix on the most modern subject of polymer gasoline with a picture of a plant and data on the product.

The book is an important contribution to the history, theory, and practice of catalysis.

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HANDBOOK OF ENGINEERING FUNDAMENTALS. Prepared by a Staff of Specialists under the Editorship of *Ovid W. Eshbach*. Volume I of Wiley Engineering Handbook Series. John Wiley & Sons, Inc., New York City, 1936. xii + 1081 pp. 576 illustrations. 14 × 21 cm. $4.00.

This book is the first volume of a set of handbooks in mechanical and electrical engineering. It has as its purpose the presentation of the fundamental material underlying all engineering. This volume is to be followed by four volumes, two in the field of mechanical engineering and two devoted to electrical engineering. All four are revisions of the existing works known to engineers by the names of their chief editors, Kent and Pender. The new set of handbooks will be less bulky and will also avoid duplicated material to a very large extent, the space formerly taken up by fundamentals being partially devoted to fuller treatment of various more specialized topics in the four volumes that follow the Eshbach text.

This volume on fundamentals includes contributions by forty different authors. At least two other competent engineers have checked each section, and the more important tables have been checked against at least two sources by different individuals.

The subject matter includes mathematical and physical tables, a fairly complete review of mathematics, and sections on physical units and standards, theoretical mechanics, mechanics of materials and of fluids, engineering thermodynamics, electricity and magnetism, radiation and light, acoustics, meteorology, chemistry, metallic and non-metallic materials, and a brief discussion of contracts.

The section on chemistry is necessarily very brief and is apparently intended only as a summary and review. It includes the common scheme of separation of metals, some discussion of electrochemistry, and a description of those elements and compounds that are of industrial importance.

Checking of this book with the current handbooks of chemistry, physics, and chemical engineering reveals somewhat less duplication than has been the case with handbooks in mechanical and electrical engineering. It supplements very admirably the handbooks used by those working in the field of chemical industry, and will probably meet a variety of needs. It is certainly a most valuable text for all engineering students.

The book is well bound in flexible covers; the type, the size of page, and the paper make it easily read; and the division into sections, each of which carries its independent sequence of page numbers, is convenient.

W. T. READ

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NEW BRUNSWICK, NEW JERSEY

THE HIGH SCHOOL SCIENCE TEACHER AND HIS WORK. *Carleton E. Preston*, Associate Professor of the Teaching of Science, University of North Carolina. McGraw-Hill Book Co., Inc., New York and London, 1936. xvii + 272 pp. 14 × 21 cm. $2.00.

"The book seeks to orient the prospective science teacher and to show how this orientation applies in various phases of his daily work. The author gives a broad view of modern teaching philosophy and indicates how this may be applied in the teaching of science by employing methods which experience has shown to be workable and effective."

In the first chapter is presented what it means to be a science teacher. This is followed by chapters on the history, the evolution, and the objectives of present-day science courses. About twenty pages are given to the choice and organization of subject matter. A short chapter on evaluating and selecting textbooks completes the treatment of the curricula of science instruction. The remainder of the book is devoted to the technics of science teaching, such as: steps in reasoning, teaching how to study various teaching methods, how to safeguard student thinking, laboratory work, the use of notebooks, manuals and workbooks, drawing in science, tests and testing, field trips, and visual aids.

At the end of each chapter are placed from two to ten challenging exercises for student report and discussion, followed by references to books and magazine articles. The references consist of: (1) books that deal with the teaching of science; (2) textbooks, workbooks, and manuals which are used in high-school classes; (3) the current literature on science teaching represented by such magazines as *Science Education*, *School Science and Mathematics*, and the JOURNAL OF CHEMICAL EDUCATION.

The presentation is clear and elementary. The treatment of the various phases of a science teacher's work is too general and too brief to cover the field in any branch of science. The chapter on testing is wholly inadequate. The student should read the references at the end of each chapter to secure a needed enrichment.

However, "the references given are not so often to reports of experimentation, that is, to the primary sources of knowledge on which advance is based, as they are to books that show how much knowledge has been summarized and evaluated, and that give help in applying it practically." The references furnished on various topics are incomplete. The journal references are worth while and up-to-date and are mainly from *Science Education* or *School Science and Mathematics*.

Certain important duties of a science teacher are not presented. There is nothing on the equipping of science laboratories; the determination of needed supplies and equipment; the ordering of supplies; the storage of supplies, etc. This information is of vital importance to the beginning science teacher, because frequently he finds this work to be his first contact with science teaching. No information is given concerning the organization and conduct of a science club. No space is devoted to the use of the library in science teaching.

There is a definite philosophy of science teaching throughout the book. This is modern and of value to the embryo science teacher.

The book in the hands of a capable and resourceful science teacher, who has had practical experience in the various branches of secondary school science, will serve as a basis for a short general course on science teaching.

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COLLATERAL READINGS IN ORGANIC CHEMISTRY. *L. A. Goldblatt*, University of Pittsburgh. Edwards Brothers, Inc., Ann Arbor, Michigan. iii + 128 pp. 5 figs. + 52 unnumbered reproductions of illustrations from various journals. 19.5 × 27 cm. $1.00.

Anyone who has taught organic chemistry to large classes will appreciate the difficulty of providing adequate library facilities for collateral journal reading. "Collateral Readings" is one satisfactory solution of this problem, and was assembled with the hope of revealing "to the student the existence of a literature of organic chemistry."

The book is a lithoprinted reproduction of articles which have appeared in American journals within the last decade, so chosen as to offer interesting collateral reading throughout the course in organic chemistry. There are articles of theoretical, historical, and industrial interest, and a satisfactory balance of the three types has been reached. The references which appear in the various articles offer to the inquiring student further opportunity for reading, and frequent supplementary references by the author serve the same purpose. It is to be regretted that the abbreviation *J. I. E. C.* is used in some of these references in place of the accepted abbreviation.

Unfortunately, the reproduction of many of the illustrations is poor. Particularly is this true when the picture represents a factory interior. We are inclined to believe that the author would not have included many of these decidedly inferior illustrations had not the method of reproduction of the printed matter made their inclusion mandatory.

The lithoprinting is well done, and the binding is satisfactory for a work of this type. Blank left pages throughout the book offer adequate space for the student to make notes.

We believe that "Collateral Readings" should prove useful, and serve the author's purpose.

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FLUORESCENCE ANALYSIS IN ULTRA-VIOLET LIGHT. J. A. Radley, M.Sc., A.I.C., and Julius Grant, Ph.D., M.Sc., F.I.C. Second Edition. D. Van Nostrand Co., Inc., New York City, 1935. xi + 325 pp. 21 figs. 23 plates, 13.5 × 21.5 cm. $7.00.

This is a revised edition following the same plan and outline as the authors' earlier (1933) book. While it contains much new material and is considerably enlarged, there are no striking differences between this and the previous edition.

According to the authors' statement in their preface to the first edition, the object of the book is to serve as a guide for practical workers "through a labyrinth of scientific papers." In accomplishing this, the contributions of over fifteen hundred papers have been tersely summarized under appropriate headings.

The first section touches briefly on the production, screening, and intensity measurement of ultra-violet light and the technic of its use in fluorescence analysis.

The second section summarizes the analytical use of ultra-violet light in nineteen different fields. The authors make no pretense of discussing any particular use or phenomenon exhaustively, but comment briefly on reported cases and follow each chapter with a complete bibliography.

To those faced by complicated and difficult analyses this book may offer suggestions for rapid determinations. To others its interest will lie chiefly in the unique and often spectacular application of the methods to minute traces of materials and in the splendid review of an extensive literature.

The book is well arranged and printed, is not marred by typographical errors, and is well illustrated. Perhaps a tendency toward loose and sweeping statements may be excused in view of the very broad character of the field covered.

WM. F. TALBOT

GUSTAVUS J. ESSELEN, INC.
BOSTON, MASSACHUSETTS

1000 AND ONE. THE BLUE BOOK OF NON-THEATRICAL FILMS. *The Educational Screen*, 64 East Lake St., Chicago, Ill. Twelfth edition, 1936–37. 152 pp. 10.5 × 18 cm. $0.75 (to *Educational Screen* subscribers, $0.25).